Effects of coagulation and calcium ions on dead end and cross-flow nanofiltrations of Natural Organic Matter (NOM)

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Effects of Coagulation and Calcium Ions on Dead-End and Cross-Flow Nanofiltrations of Natural Organic Matter (NOM)

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Submitted in Fulfillment of the
Requirements for the Degree
Doctor of Philosophy

2011

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ABSTRACT

Nanofiltration (NF) technology has been widely used in drinking water treatment process and advanced wastewater reclamation due to its capability in effectively removing contaminants down to multivalent ions, while operating at lower pressure compared to reverse osmosis (RO). One of the major challenges in membrane filtration is fouling, since fouling deteriorates the performance of nanofiltration over time. Although many types of foulant can cause fouling, natural organic matter (NOM) is considered as a major foulant due to its recalcitrant properties and the fact that it is commonly found in natural water. In addition to this, the presence of divalent cations such as calcium could add the severity of fouling, as it is capable of forming bonds between NOM and between NOM-membrane surface.

In water treatment processes, NOM is commonly removed by coagulation/flocculation using coagulant such as alum. Coagulation is also used as pre-treatment prior to membrane filtration, or used in conjunction with membrane filtration. Hybrid coagulation-nanofiltration is a technology that combines coagulation and nanofiltration as a part of drinking water treatment or advanced wastewater reclamation. This technique is found to effectively remove NOM while producing high permeate quality and quantity. Although many studies have looked into the interaction between NOM and calcium or the performance of membrane filtration with coagulation pre-treatment, none have attempted to investigate the interaction between foulant-foulant and membrane-foulant when NOM, calcium and coagulant are co-occurring. In addition to this, there exists a discrepancy between the observed permeate flux decline during filtration of sodium alginate, which is commonly used to model high molecular weight NOM, in the presence of calcium; while some studies reported that calcium ions were responsible for severe permeate flux decline, others reported that the permeate flux was improved in the presence of calcium.

This study systematically investigated the interaction between NOM and calcium in the presence of coagulant. Permeate flux trends, permeate quality, feed characteristics

and resistances were examined in order to delineate the interactions and fouling mechanisms in these systems. Purified Aldrich Humic Acid (PAHA) and sodium alginate were used as model NOMs, and filtration experiments were conducted using both dead-end and cross-flow nanofiltration configurations. A conceptual model of NOM interaction with calcium and coagulant was proposed in order to explain the fouling phenomena. Lastly, the added value of combining coagulation and nanofiltration (Hybrid Coagulation-Nanofiltration) was explored by using this technique to remove disinfection by-products (DBPs) alongside NOM.

It was found that permeate flux was significantly improved with the addition of coagulant despite the presence of calcium, as the resistances were lowered. For both PAHA and sodium alginate, coagulation increased the foulant attachment on membrane, altered the cake characteristics into more compressible and resulted in two or more fouling mechanisms occurring at the same time. The presence of calcium resulted in a more compact and dense fouling layer, leading to severe permeate flux decline during filtration of PAHA, but an opposite effect was observed during filtration of sodium alginate. While calcium ions could change the conformation of PAHA into more coiled and hence compact the resulting cake layer, the resulting gel layer formed by sodium alginate and calcium was permeable. The interaction between sodium alginate and calcium, however, is influenced by ionic strength and concentration ratio between the two solutes. It was further suggested that the different filtration configurations (i.e. dead-end or cross-flow) could create different conditions at the boundary layer for this interaction such that the observed permeate flux trends might differ.

In the study of hybrid coagulation-nanofiltration of PAHA with bromide/bromate as the chosen contaminants, it was found that PAHA was effectively removed and bromate was reduced, while high permeate flux was maintained when ferrous sulphate coagulant was used. Removal of bromide prior to the formation of bromate was found to be impractical since bromide was poorly removed by coagulation, nanofiltration, or hybrid coagulation-nanofiltration. As membrane filtration and coagulation have been widely applied in water treatment processes, these results indicate that the application of hybrid coagulation-nanofiltration for removal of NOM and bromate could be feasible by choosing the suitable membrane and coagulant.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AFM	atomic force microscopy
AHA	Aldrich humic acid
CF	cross-flow
CP	concentration polarization
DBP	disinfection by products
DE	dead-end
DI	deionized
EfOM	effluent organic matter
EPS	extracellular polymeric substances
HA	humic acid
IC	ion chromatography
ICP-OES	inductively coupled plasma with optical emission spectrophotometry
LPRO	low pressure reverse osmosis
MCL	maximum contaminant level
MF	microfiltration
MFI	membrane fouling index
NF	nanofiltration
NOM	natural organic matter
PAHA	pre-treated Aldrich humic acid
RO	reverse osmosis
SA	sodium alginate
SEM	scanning electron microscopy
SMP	soluble microbial products
TFC	thin-film composite
TMP	trans-membrane pressure
TOC	total organic carbon
UF	ultrafiltration

USEPA	United States environmental protection agency
UV	ultraviolet

Symbols

A	effective membrane area (m^2)
a	model parameter in blocking filtration law (gradient)
b	model parameter in blocking filtration law (interception)
C_b	bulk concentration (kg m^{-3})
d	particle diameter (m)
I	fouling index (m^{-2})
J	permeate flux ($\mu\text{m s}^{-1}$)
J_0	clean water flux ($\mu\text{m s}^{-1}$)
J'	permeate flux after adsorption step ($\mu\text{m s}^{-1}$)
K''	empirical Kozeny constant (-)
M	mass of deposited cake (kg)
m_f	specific accumulated mass = M/A (kg m^{-2})
n	cake compressibility factor (-)
ΔP	trans-membrane pressure (kPa)
R_a	resistance due to adsorption (m^{-1})
R_c	resistance due to cake formation (m^{-1})
R_d	resistance due to deposited materials on membrane surface (m^{-1})
R_m	membrane hydraulic resistance (m^{-1})
R_p	resistance due to pore blocking (m^{-1})
R_t	total resistance (m^{-1})
t	filtration time (s)
V	total filtrate volume (mL)

Greek letters

α	specific cake resistance (m kg^{-1})
α_c	specific cake resistance as a function of ΔP_c (m kg^{-1})
α_0	specific cake resistance at the absence of pressure difference (m kg^{-1})
α_{emp}	empirical specific cake resistance (m kg^{-1})
α_{MFI}	experimental specific cake resistance (m kg^{-1})

δ	cake thickness (μm)
ε	porosity (-)
γ	attachment coefficient (-)
γ_{PB}	attachment coefficient during pore blocking (-)
γ_C	attachment coefficient during cake formation without compression (-)
γ_{CC}	attachment coefficient during cake formation with compression (-)
λ	wavelength (nm)
η	dynamic viscosity (Pa.s)
ρ	particle density (kg m^{-3})

Chapter 1

Introduction

1.1 Background

As the demand of fresh water is constantly rising while raw water sources have become increasingly scarce, advanced wastewater reclamation for potable water purposes has been considered and even performed in some countries. One of the options to produce high quality water is by integrating membrane technology such as nanofiltration or reverse osmosis in water treatment system. Membrane filtration has been developing rapidly since its emergence in the 1960s (Schäfer *et al.* 2005). Compared to conventional water treatment, membrane technology offers smaller footprint and easier up scaling. As time progresses, the capital cost of applying this technology is lessening, making it economically more feasible.

Membrane processes in drinking water treatment and advanced wastewater reclamation include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis, membrane electrolysis, diffusion dialysis, and dialysis (Mulder 1996).

Nanofiltration has been gaining attention as the polishing step in water treatment technology since 20 years ago (Hilal *et al.* 2004; Nystrom *et al.* 1995). Nanofiltration, also known as Low Pressure Reverse Osmosis (LPRO), has characteristics halfway between ultrafiltration and reverse osmosis. The intermediate molecular weight-cut off (MWCO) of nanofiltration membrane allows rejection of smaller and charged

molecules relative to ultrafiltration with higher permeate water flux relative to that of a reverse osmosis membrane. This technology can be employed to produce a large quantity of high-quality water in drinking water treatment and to reclaim wastewater effluents.

Nanofiltration still suffers from major problems such as membrane fouling. Fouling is defined as the accumulation of particles (or 'foulant') along membrane surface and/or within the membrane pores (Schäfer *et al.* 2005). It is widely known that fouling causes decline in permeate water flux over time at constant applied pressure. As a result, the system must be operated at an increasingly elevated pressure in order to maintain constant permeate flux, which will lead to even more severe fouling. Previous studies have shown that rate and extent of fouling are determined by a number of parameters such as feed water composition, membrane properties and operational conditions, all of which promote membrane-foulant and foulant-foulant interactions (Li and Elimelech 2004). Although periodic membrane cleaning will restore the permeate flux, membrane replacement will eventually be inevitable. This means that efforts made to control and alleviate membrane fouling will result in the improvement of membrane performance.

Foulants can be categorized into several groups such as sparingly soluble (inorganic) salts, organic substances, colloidal and particulate matter and biological growth, among which organic matter is considered to be the principal cause of membrane fouling (Cohen and Probstein 1986; Wiesner and Chellam 1999). Organic matter may be naturally present in drinking water sources or synthetically produced from domestic activities (Shon *et al.* 2006). In addition to this, divalent ions that have a strong potential to form complexes with organic matter are capable of forming bridges between membrane surface and organic matter (Lee *et al.* 2006; Lee and Elimelech 2006; Li and Elimelech 2004; Tang *et al.* 2007b). These divalent ions include calcium (Ca^{2+}) and magnesium (Mg^{2+}), and are present naturally in raw water (Sposito 1989). Some studies have suggested that these ions are responsible for severe fouling and significant decrease of permeate flux during filtration of natural organic matter (NOM) (Ang and Elimelech 2007; Katsoufidou *et al.* 2007b; Lee and Elimelech 2006; Li and Elimelech 2004; Tang *et al.* 2007b), which is commonly

modeled by humic acid for low molecular weight organics and sodium alginate for high molecular weight organics.

In drinking water treatment trains, organic matter is commonly removed via coagulation/flocculation process using coagulants such as aluminum, and the flocs formed are removed via filtration. In membrane filtration, coagulation as a mean of pre-treatment offers advantages such as reduction of coagulant dose, mixing-time, energy consumption and head loss, and has been shown to effectively remove organic matter while maintaining high flux recovery (Lee *et al.* 2000; Schäfer May 2001; Shon *et al.* 2005). Some studies have considered combining coagulation and membrane filtration processes (hybrid coagulation-nanofiltration), and found significant improvement in permeate flux and organic removal when using ultra- and microfiltration (Guigui *et al.* 2002; Jung *et al.* 2006; Kim *et al.* 2006; Kimura *et al.* 2008; Lahoussine-Turcaud and Wiesner 1990; Seockheon *et al.* 2006). Although the use of aluminum coagulant in drinking water treatment has shown to be effective in removing organic matter, it does not prevent the accumulation of flocs along membrane surface leading to membrane fouling. Furthermore, the presence of calcium ions will complicate the interaction between NOM and coagulant, and between foulant and membrane.

While drinking water regulations have become more stringent, more emerging contaminants have been identified and less space is available in cities where municipal drinking water and advanced wastewater reclamation are located. There is an urgent need of a novel technology that does not only produce high quality and quantity water, but also requires only a small footprint. This thesis is reporting the interaction between NOM and calcium ions in the absence and presence of coagulants, while looking at the possibilities of applying hybrid coagulation-nanofiltration in water treatment and exploring the added values of this technique in removing other contaminants. Information on the interaction of organic matter with calcium ions in the presence of coagulant and its relation to the rate of nanofiltration membrane fouling will provide insights on the optimum condition for organic matter coagulation while reducing the fouling potential. In addition, hybrid coagulation-nanofiltration offers the advantages mentioned above while only requiring a simple modification of the available treatment processes.

1.2 Objectives and Significance

As membrane filtration goes hand-in-hand with fouling, membrane-fouling phenomenon is always of interest to researchers. Interaction between NOM and divalent ions, which are naturally present in raw water, adds another level of complexity to the filtration system. In addition to this, coagulation process changes the dynamics of the system. By understanding the fouling mechanism of NOM in the presence of other substances such as divalent cations and coagulants, the fouling mitigation techniques such as hybrid coagulation-nanofiltration could be improved.

The specific objectives of this research are:

1. To systematically investigate the fouling mechanism and the corresponding resistances in systems containing NOM, calcium ions and aluminum-based coagulants and their combinations.
2. To delineate the interaction between sodium alginate molecules and calcium ions, and their consequences in filtration of solutions in dead-end and cross-flow nanofiltration configurations.
3. To investigate the added value of hybrid coagulation-nanofiltration in removing disinfection by-products (DBPs) such as bromate and bromide.

Significance and benefits of this research

These fundamental studies of membrane fouling will provide insights that can be employed to help mitigate membrane fouling. In particular, this research can contribute to the improvement of permeate flux, development of new fouling control technology, and optimization of membrane filtration condition and cleaning strategies. Hybrid coagulation-nanofiltration technique developed in this research could decrease the footprint of a water treatment plant by eliminating the sedimentation step, in addition to effectively remove NOM and other contaminants while maintaining high permeate flux.

1.3 Scope

This thesis is divided into eight chapters and six appendices, with four chapters as the main body of the thesis. Chapter 2 outlines the literature review with an emphasis on the previous studies and major findings in this field. Chapter 3 delineates the materials and methods used in this study, and Chapter 8 concludes the study and lists the recommendations for further research. The main body of this thesis is Chapters 4-7, which are taken from published and submitted articles listed below:

- Chapter 4 discusses the fouling mechanisms and flux decline trends in filtrations of low molecular NOM (humic acid), calcium, alum coagulant and their combinations. This article is published in the Journal of Membrane Science in February 2009, with a title of “Organic fouling of nanofiltration membranes: Evaluating the effects of humic acid, calcium, alum coagulant and their combinations on the specific cake resistance”, co-authored by Darren D. Sun and James O. Leckie.
- Chapter 5 focuses on fouling mechanisms and their corresponding resistances in dead-end nanofiltration of high molecular weight NOM (sodium alginate), in the presence of calcium and alum coagulant. This article is published in the Journal of Membrane Science in August 2009, with a title of “Fouling mechanism and resistance analyses of systems containing sodium alginate, calcium, alum and their combination in dead-end fouling of nanofiltration membranes”, co-authored by Wei Chun, Darren D. Sun and James O. Leckie.
- Chapter 6 looks into fouling in cross-flow nanofiltration of sodium alginate, calcium, alum and their combination, and focuses on sodium alginate – calcium interaction. This article has been accepted for publication in the Journal of Membrane Science in December 2010, with a title of “Systematic study on calcium-alginate interaction in a hybrid coagulation-nanofiltration system”, co-authored by Tan Li Hui, Darren D. Sun and James O. Leckie.

- Chapter 7 investigates the potential application of hybrid coagulation-nanofiltration technique in removing bromide/bromate, humic acid while maintaining the permeate flux using two different types of nanofiltration membranes and coagulants. This article is published in the Journal of Membrane Science in December 2010, with a title of “Hybrid coagulation-nanofiltration membrane for removal of bromate and humic acid in water“, co-authored by Tor Jia Tong, Darren D. Sun and James O. Leckie.

The appendix section provides additional information to the main chapters. Appendix A consists of the calibration curves for determination of alginate and humic acid concentrations, as well as solution's ionic strength. Appendix B provides supplemental data for Chapter 5. Appendix C discusses the calculation of calcium to G residue ratio with regards to Chapter 6. Appendix D provides the information on characteristics of bromide and bromate. Appendix E discusses the cake characterization of sodium alginate, calcium and alum systems, and is a continuing study of Chapter 5. This section is taken from an article submitted to Water Science and Technology: Water Supply in November 2009, co-authored by Darren D. Sun and James O. Leckie. Appendix F is an early study on the effects of coagulant concentration, calcium and settling on hybrid coagulation-nanofiltration. This section was presented at the International Conference on Membranes (ICOM) in February 2008, and co-authored by Darren D. Sun and James O. Leckie.

Chapter 2

Literature Review

2.1 Membrane Filtration and Fouling Phenomena

Membrane filtration is defined as a separation process in which membrane is used to separate one component from a fluid through various mechanisms (e.g. size exclusion, charge repulsion, diffusion, etc). The use of membrane filtration as a separation technique has been known as early as 1920, when microfiltration was used to filter bacteria (Mulder 1996). First generation of membrane which includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been widely used in different applications such as drinking water and wastewater treatments, desalination, and ultra-pure water production for use in various industries.

In general, membrane filtration operation is divided into two configurations: cross-flow and dead-end. Figure 2.1 shows a schematic of cross flow membrane operation, where feed water enters the system parallel to the membrane (left), permeate flux flows through the membrane (bottom), while retentate flux exits the system parallel to the membrane (right); large particles retained by the membrane will accumulate at the membrane surface and form fouling layer. Dead-end configurations do not have retentate flow, since all of the feed water passes perpendicularly through the membrane and hence generates only permeate. While cross-flow is the most commonly used configuration in drinking water and wastewater treatment trains,

the use of dead-end configuration could be cost effective when filtering feed water with low foulant concentration (Ven *et al.* 2008).

Nanofiltration membranes

Nanofiltration, defined as a process with characteristics between those of ultrafiltration and reverse osmosis, is now an emerging technology in drinking water treatment and wastewater reclamation. This technology has been employed to remove impurities such as salts, hardness, pathogens, turbidity, disinfection-byproduct (DBP) precursors, pesticides and other potable water contaminants (Lee *et al.* 2005d; Schäfer *et al.* 2005). The process of employing these membranes is considered very attractive due to its distinctive feature of retaining charged particles down to the size of multivalent ions at a lower pressure compared to that of RO (Mulder 1996).

NF membranes exhibit two important features of separation. First, it is capable of rejecting bivalent or higher charged anions like sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) as well as multivalent ions, while allowing a partial transmission of monovalent ions. Second, it is capable of rejecting low molecular weight organics. The mechanism behind these features is based on steric (size) hindrance and electrostatic (charge) repulsion (Bruggen *et al.* 2003; Seidel *et al.* 2001). In addition, electrostatic repulsion may affect membrane structure and permeability by altering the membrane pore size (Braghetta *et al.* 1997).

Figure 2.1 Schematic of cross-flow membrane filtration.

2.1.1 Membrane fouling and foulants

One of the major obstacles in membrane filtration is fouling. Fouling is defined as the accumulation of substances on membrane surface and/or within membrane pores which results in deterioration of membrane performance (Schäfer *et al.* 2005). Fouling may cause decline in both flux quantity and quality, and eventually lead to a shorter membrane life. It has been reported that sparingly soluble (inorganic) salts (e.g. CaCO_3 , CaSO_4 , SiO_4), organic substances (e.g. protein, natural organic matter, polysaccharides), colloidal and particulate matter (e.g. aluminum oxide, clay, silt), and biological growth on membrane surface due to attachment of microorganisms (Cohen and Probstein 1986; Schäfer *et al.* 2005; Seidel and Elimelech 2002) are the common NF membrane foulants.

Figure 2.2 Typical membrane fouling cleaning protocols as adopted from Schäfer *et al.* (2005).

2.1.2 Membrane fouling mechanisms

In general, membrane fouling can be divided into two main groups: (1) reversible fouling, and (2) irreversible fouling. As shown in Figure 2.2, water flux decreases as

foulant is introduced into the system until it reaches a steady state. Membrane cleaning techniques such as water flushing will recover some of the flux, whereas chemical cleaning often recovers most, if not all, of the flux. Schäfer et al. (2005) suggested the term ‘irreversible fouling’ for the condition where there is a difference between the initial clean water flux and the flux after chemical cleaning. They further suggested that reversible fouling can be ‘reversed’ by changing the operating conditions, without attempting any membrane cleaning.

Membrane fouling occurs via different mechanisms. Belfort et al. (1994) divided the fouling mechanism of microfiltration (MF) membranes based on the particle size dependence of foulant, which can be applied to NF membranes. It is also possible to have all kinds of fouling mechanisms occurring at the same time when the foulant is polydisperse. In addition, gel layer formation may occur when organic solutes accumulate on the membrane surface and their concentration along the membrane wall exceeds the solubility. Flux decline due to various fouling mechanisms can be described by the Resistance in Series Model as adopted from Schäfer et al. (2005) as follows:

$$J = \frac{\Delta P}{\eta(R_m + R_a + R_p + R_c)} \quad (2.1),$$

where R_m denotes the clean membrane resistance, where R_a , R_p , and R_c denote the added resistance due to adsorption, internal pore plugging, and cake formation respectively. This equation can be used to calculate the resistances of a fouled membrane.

2.1.3 Modified fouling index (MFI)

The modified fouling index (sometimes also referred to as ‘membrane filtration index’ or ‘membrane fouling index’) was first introduced by Schippers and Verdouw (1980) in order to correlate the Silt Density Index (SDI) to the concentration of foulant as a measure of fouling tendency. Schippers and Verdouw divided the fouling

mechanism that may occur during filtration into four different mechanisms: (1) depth filtration, (2) blocking filtration, (3) cake filtration without compression, and (4) cake filtration with compression. The MFI equation was derived based on cake filtration mechanisms and their associated assumptions:

$$\frac{dV}{dt} = \frac{1}{\eta} \frac{\Delta P \cdot A}{R_m + R_c} \quad (2.2)$$

where R_m and R_c are the membrane resistance and cake resistance per unit area, respectively, and A is the surface area of the filter. Assuming that there is no cake compression:

$$R_c = \frac{V}{A} I \quad (2.3)$$

where I is the fouling index, which is a measure of the fouling potential of the feed water. After combining Equations (2.2) and (2.3) and integrating the combined equation from $t = 0$ to $t = 1$ at constant ΔP , the MFI equation is obtained:

$$\frac{t}{V} = \frac{\eta I}{2\Delta P A^2} V + \frac{\eta R_m}{\Delta P A} \quad (2.4).$$

Specific cake resistance, α , is defined as the cake resistance, R_c , normalized by the accumulated cake mass per unit of membrane area (Lee *et al.* 2000):

$$\alpha = \frac{R_c}{(M/A)} = \frac{R_c A}{V C_b} \quad (2.5),$$

where M is the mass of cake deposited on membrane surface, A is the effective area of membrane, and C_b is the bulk concentration of particles. Specific cake resistance, α , could also be calculated by dividing the fouling index, I , with the bulk concentration of organic foulant in the feed solution, C_b (Lee *et al.* 2000; Schippers and Verduw 1980):

$$\alpha = \frac{I}{C_b} \quad (2.6).$$

According to the Carman-Kozeny equation, α is inversely proportional to cake porosity to the power of three, or:

$$\alpha = \frac{180(1 - \varepsilon)}{\rho d^2 \varepsilon^3} \quad (2.7),$$

where ρ is the particle density and d is the mean diameter of particles. Schippers and Verdouw (1980) developed a theory of cake filtration, where particles are retained on membrane by a mechanism of surface deposition. When cake compression is present during filtration, the cake compressibility factor can be calculated using the following equation:

$$\alpha_c = \alpha_0 \Delta P^n \quad (2.8),$$

where α_c is the specific cake resistance as a function of trans-membrane pressure (ΔP), and α_0 is the specific cake resistance at the absence of pressure difference. If cake compression occurs, the first term of the right hand side of the MFI equation changes gradually according to the pressure, and the MFI equation becomes:

$$\frac{t}{V} = \frac{\eta I (1 + \Delta P^a)}{2 \Delta P A^2} V + \frac{\eta R_m}{\Delta P A} \quad (2.9),$$

where a is a constant which is dependent on the compressibility of the colloids, and:

$$\frac{\Delta P \times \eta I}{2 \Delta P A^2} = \Delta P \times \tan \theta = \text{cons} \tan t \quad (2.10),$$

where θ is the slope of the MFI curve during cake filtration without compression (see discussion in the following paragraph and Figure 2.3).

Figure 2.3 The MFI plot of t/V (ratio of filtration time to the filtrate volume) as a function of filtrate volume (V) (Schippers and Verdouw 1980). (I) denotes the blocking filtration region, (II) and (III) denote the cake filtration without compression and cake filtration with compression regions, respectively.

Furthermore, when a plot of the ratio of time to the filtrate volume (t/V) as a function of the filtrate volume is constructed as shown in Figure 2.3, fouling mechanisms that occur during filtration can be depicted. In this figure, three fouling mechanisms occur consecutively: (I) blocking filtration, (II) cake filtration without compression, and (III) cake filtration with compression.

Schippers and Verdouw (1980) listed some limitations of this equation: while the SDI was derived based on dead-end filtration setup, the MFI equation will not be completely accurate when applied to cross-flow setup. This is because the rate of deposition of particles (possibly of different sizes) will not be accounted for in this equation. In addition to that, the accumulation of particles on the membrane surface will be highly alleviated in cross-flow setup due to the cross flow.

2.1.4 Factors promoting fouling

Numerous researchers have addressed the factors that promote fouling. Feed water composition (e.g. foulants, pH, ionic strength, divalent cations), membrane properties (e.g. charge, surface roughness, hydrophobicity, surface chemistry), and operational conditions (e.g. flux, crossflow velocity, temperature) are known to contribute to membrane fouling (Childress and Elimelech 1996, 2000; Faibish *et al.* 1998; Lipp *et al.* 1994; Seidel and Elimelech 2002; Zhu and Elimelech 1997). Adding complexity to the system, these factors are known to be inter-dependent; for example, changing the solution pH will result in the alteration of membrane surface charge, possibly membrane pore size (Braghetta *et al.* 1997), and the conformation of organic foulant (Hong and Elimelech 1997).

The interplay between hydrodynamic and electrostatic forces is found to highly affect foulant transport to the membrane surface in cross-flow filtration (Seidel and Elimelech 2002). Palecek and Zydney (1994) suggested that in a cross-flow filtration system, forces acting on a protein in the bulk solution include (1) permeation drag force that carries the protein toward membrane surface, and opposing forces which consist of (2) electrostatic and (3) other forces of interaction such as dipole-dipole interactions and hydration forces. Seidel and Elimelech (2002) found that membrane fouling by NOM is governed by the coupled influence of chemical and hydrodynamic interactions which include initial permeate flux, calcium complexation, permeation drag, and shear rate (crossflow velocity). They suggested that fouling mitigation and control may be achieved through optimization of these parameters.

2.2 Natural Organic Matter (NOM)

NOM is considered as a major membrane foulant due to its recalcitrant properties and the fact that it is ubiquitous in natural waters (Brant and Childress 2002; Seidel *et al.* 2001). It is predominantly composed of organic macromolecules with humic substance characteristics, often found as negatively charged in aqueous solution at neutral to high pH. These substances comprise of carboxylic (-COOH) and/or

phenolic (-OH) functional groups which are deprotonated under such pH condition (Hong and Elimelech 1997; Sander *et al.* 2004; Sposito 1989).

Figure 2.4 Schematic illustration of effect of solution chemistry on NOM configuration and the resulting fouling layer formed on membrane surface (Hong and Elimelech 1997).

Numerous studies have addressed the physical and chemical properties of NOM fouling on membrane surfaces. Seidel and Elimelech (2002) stated that NOM fouling of NF membranes is influenced by a combination of many parameters such as initial permeate flux, crossflow velocity, and divalent ion concentration. Braghetta *et al.* (1997) found that permeate flux and NOM rejection decrease significantly at a low pH and high ionic strength due to the charge screening of electrostatic double layer of both membrane surface and NOM, whereas Hong and Elimelech (1997) suggested that solution chemistry affects the conformation of NOM in solution, thus leading to different characteristics of fouling layers formed on membrane surface. According to Hong and Elimelech (1997) and as shown in Figure 2.4, NOM in solution will have a coiled and compact configuration at high ionic strength, low pH or in the presence of divalent cations which will result in compact, dense, and thick fouling layer that leads to severe permeate flux decline; at low ionic strength, high pH and in the absence of divalent cations, NOM will have a linear configuration that forms loose, sparse, and thin fouling layer that leads to small permeate flux decline. In addition, fouling by NOM could impact the micro-pollutant transports during membrane filtration (Broeckmann *et al.* 2005; Steinle-Darling *et al.* 2007).

Figure 2.5 Schematic illustration of calcium ions influence on the binding of NOM surrogate on clean membrane surface as adopted from (Li and Elimelech 2004).

2.2.1 Interaction between NOM and divalent cations

Divalent cations such as calcium and magnesium may neutralize the negatively-charged organic molecules when they are present in the system, leading to a dense fouling layer (Lee and Elimelech 2006; Li and Elimelech 2004; Tang *et al.* 2007b). In addition, they are known to form complexes with these organic molecules (Li and Elimelech 2004; Tang *et al.* 2007b). As shown schematically in Figure 2.5, calcium acts as a bridge between the membrane and NOM which results in a cross-linked organic fouling layer (Li and Elimelech 2004).

A number of studies have been conducted to investigate the effect of divalent ions on NOM fouling of various membranes, some of which are summarized in Table 2.1. An earlier study by Childress and Elimelech (1996) shows that divalent cations affect the membrane surface charge more substantially than divalent anions. Zhu and Elimelech (1997) and Lee *et al.* (2005a) both found similar results that calcium ions do not interact with silica colloids, whereas calcium interaction with NOM results in severe flux decline. It is important to note that the foulant model used in both studies was stable (i.e. did not aggregate) at the concentration range of calcium added to the systems.

Table 2.1 Research on effect of divalent cations on NOM fouling of membranes.

Investigator(s)	Type of membrane	Foulant(s)	Ranges of parameters	Remarks
Childress and Elimelech (1996)	RO and NF	n/a	0.001 M CaCl_2 , Na_2SO_4 , and MgSO_4 ; pH 2-9; 0.01 M NaCl	Evaluates the effect of divalent cations on membrane surface charge
Zhu and Elimelech (1997)	RO	Silica colloids	0.01 M NaCl; 0.0001-0.01 M CaCl_2 ; 30mg/L particle conc.; pH 5.4-5.6 or 7.8	Silica colloids are stable at the calcium conc. range
Schäfer et al. (1998)	NF	SRHA, Suwanee River Fulvic Acid (SRFA), Australian NOM	SRHA conc. 12.5mg/L; SRFA conc. 5mg/L; 0.5-2.5mM Ca^{2+} ; 1mM NaHCO_3 ; 20mM NaCl; pH 4,8,10	Precipitation of calcium-organic complex may occur, lower flux at higher calcium concentrations
Seidel and Elimelech (2002)	NF	Humic acid	0.1-1.0 M Ca^{2+} ; 4.0-80.0 cm/s cf; IS 10 mM; pH 8.0	More severe flux decline at higher calcium conc.
Shim et.al (2002)	NF and UF	Nakdong River NOM	0.01 M NaCl, KCl, CaCl_2 , MgCl_2	Electrophoresis method
Li and Elimelech (2004)	NF	Suwanee River humic acid (SRHA)	IS 10-100 mM; pH 8.1; 20mg/L SRHA; 1 mM Ca^{2+} or Mg^{2+}	Interfacial forces measurement using AFM
Broeckmann et al. (2005)	NF	Particulate cellulose, colloidal MCC	MCC conc. 0.07g/L; Tap water: 16mg/L Ca^{2+} , 8 mg/L Na^+ , pH 7.7, conductivity 130 $\mu\text{S}/\text{cm}$	Sodium (and possibly calcium) influences the irreversible fouling at low and high pH
Lee et.al. (2005a)	NF	Silica colloids, Nakdong River NOM	0.3 mM Ca^{2+} ; IS 10 mM; pH 8.1; NOM conc.20mg/L; colloid conc. 200mg/L	Less severe flux decline for combined NOM-colloids than added individuals
Li and Elimelech (2006)	NF	SRHA	1 mM Mg^{2+} or Ca^{2+} ; IS 10 mM; pH 8.1; colloid conc. 20mg/L; SRHA conc. 100mg/L	More severe flux decline for combined NOM-colloids than added individuals
Lee and Elimelech (2006)	RO	Alginate, SRHA	0.5 mM Mg^{2+} or Ca^{2+} ; IS 10mM; pH 6.0; alginate 20mg/L	Interfacial forces measurement using AFM
Tang et.al. (2007b)	RO and NF	Purified aldrich humic acid (PAHA)	PAHA conc. 2-20mg/L; pH 4.5-7.0; 0-1 mM Ca^{2+}	Thicker, denser fouling layer when calcium is present

Seidel and Elimelech (2002), Lee and Elimelech (2006) and Tang et al. (2007b) found that a more severe flux decline occurs when both calcium and NOM are present in the system as compared to the individual foulants. Schäfer et al. (1998) and Broeckmann et al. (Broeckmann *et al.* 2005) also found similar results, while Schäfer et al. suggested that precipitation of complex organic-calcium may occur during filtration.

The role of divalent cations in charge neutralization and/or bridging between membrane and NOM are shown in studies by Li and Elimelech (2004) and Tang et al. (2007b). Effect of combined fouling of colloids and NOM in the presence of divalent ions is shown in similar studies by Lee et al. (2005d) and Li and Elimelech (2006). It is interesting to note that the studies show contradicting results; Lee et al. (2005d) observed a less severe flux decline when both foulants were present compared to the sum of flux decline of the individual ones, whereas Li and Elimelech (2006) found the combined fouling to be more severe.

2.2.2 Humic acid as model NOM

Figure 2.6 Molecular structure of humic acid (Stevenson 1982).

Humic materials are abundant and commonly found in natural waters as a degradation product of carbohydrate, protein, lignin etc. It is suggested by Ghosh and Schnitzer (1980) that humic materials are long-chained molecules with possible cross-linking and coiled conformation at high ionic strength, low pH or high concentration of sample. This shows that humic acid properties are highly influenced by the bulk solution conditions. The charge of humic molecules comes from deprotonation of carboxylic (COOH) and phenolic (OH) functional groups and may result in repulsion and expansion of the coil (Stevenson 1982). Humic substances can be divided into three groups: fulvic acid, humic acid and humin. Fulvic and humic acid are the major components of NOM, with molecular weights ranging from 100 to 4,000 Da and

10,000 to 50,000 Da, respectively. While fulvic acid is soluble at a wide pH range, humic acid is only soluble at pH larger than 2.

Humic acid has been used extensively in membrane filtration studies to investigate membrane fouling by NOM (Amy and Cho 1999; Cho *et al.* 2000; Hong and Elimelech 1997; Listiarini *et al.* 2009c; Tang *et al.* 2007b, c; Yoon *et al.* 1998). Molecular structure of humic acid is shown in Figure 2.6. Some researchers obtained the humic materials from natural sources such as rivers (Lee *et al.* 2005a; Lee and Elimelech 2006; Li and Elimelech 2006), others purchased the commercially available humic acid from Sigma-Aldrich (Listiarini *et al.* 2009c; Tang *et al.* 2007b). Aldrich humic acid (AHA) is well characterized and hence commonly used as model foulant. However, extensive pre-treatment is needed to remove the fulvic, metal and ash content from AHA (refer to Section 3.1.2 of the Materials and Method chapter).

2.2.3 Alginate as model NOM

Figure 2.7 Molecular structure of sodium alginate (Katsoufidou *et al.* 2007a).

Sodium alginate is hydrophilic polysaccharides, which is produced by algae and bacteria, consisting of two repeating polymers: β -D-mannuronic acid and α -L-guluronic acid residues (Katsoufidou *et al.* 2007a). The molecular structure of alginate is shown in Figure 2.7. Similar to humic acid, the physical and chemical properties of alginate are highly influenced by the solution condition (pH, ionic strength, concentration of sample). Deprotonation of carboxylic functional group of sodium alginate results in negatively charged molecules at pH around neutral. This

leads to the expansion of polymer due to the repulsive forces of the chain, which is also observed in humic acid.

Sodium alginate has been commonly used by researchers to model polysaccharides since it has characteristics of and behaves similarly to extracellular polymeric substances (EPS) during filtration (Lee *et al.* 2006; Ye *et al.* 2005). EPS are produced by biomass that may be present naturally in drinking water sources, which is one of the main causes of organic fouling and biofouling (Shon *et al.* 2006).

Figure 2.8 Schematic illustration of the egg-box model (Katsoufidou *et al.* 2007a).

In the presence of calcium ions, sodium alginate forms a highly organized gel-like structure which resembles an egg-box (Grant *et al.* 1973). This theory was proposed by Grant *et al.* (1973) and the structure was called the “egg-box model”. They suggested that the cooperative mechanism between calcium ions sodium alginate involves preferential binding of calcium ions to the phenolic functional group of sodium alginate molecules, as schematically shown in Figure 2.8. Sodium alginate molecules which are adjacent to each other may stack together with the aid of calcium ions, forming a gel network that looks like an egg box. This dense gel network is

suggested by many researchers to be responsible for severe permeate flux decline during membrane filtration of feed solutions containing sodium alginate and calcium (Ang and Elimelech 2007; Katsoufidou *et al.* 2007a; Lee and Elimelech 2006). However, some researchers found that the presence of calcium could improve the permeate flux during alginate filtration (Listiarini *et al.* 2009c; Ven *et al.* 2008), due to the ability of calcium in inducing the formation of highly permeable polysaccharide gel layer (deKerchove and Elimelech 2007).

2.3 Aluminum Coagulant in Drinking Water Treatment

In aqueous solution, aluminum hydrolyses and polymerizes into different species depending on the solution pH and the total concentration of aluminum (Bi *et al.* 2004; Sposito 1989; Zhang *et al.* 2004). At low ratio of OH/Al (<0.5) and low concentration of total aluminum, monomeric aluminum species are formed following these reactions:

At a higher OH/Al ratio (0.5-2.5), polymerization of aluminum occurs and various polymeric species such as $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ are formed. However, the predominance and nature of these metastable larger polymeric species are still questionable (Sposito 1989; Wang *et al.* 2003). Upon increasing the OH/Al ratio, aluminum precipitates, $\text{Al}(\text{OH})_3$, are formed following the reaction:

At much higher pH, dissolution of $\text{Al}(\text{OH})_3$ precipitates may occur, forming negatively charged aluminum monomers, $\text{Al}(\text{OH})_4^-$, following the reaction:

Aluminum-based coagulants such as aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, also known as alum) and polyaluminum chloride (PACl) are commonly used in drinking water treatment plants to remove particulates, colloids, and dissolved substances (Benschoten *et al.* 1994; Srinivasan *et al.* 1999). Four different mechanisms that promote coagulation may occur depending on the degree of interaction between coagulant and particles, which include: (1) compression of electrostatic double layer, (2) alteration of surface charge, (3) inter-particle bridging, and (4) enmeshment in precipitated solids (Benschoten *et al.* 1994; Gregor *et al.* 1997). These mechanisms also hold for the removal of high molecular weight colloidal NOM (Gregor *et al.* 1997).

When aluminum is used as a coagulant, monomeric species of aluminum will be responsible for electrostatic double layer compression and possibly altering the surface charge of NOM, while polymeric and $\text{Al}(\text{OH})_3$ precipitates will remove NOM via interparticle bridging and sweep flocculation (enmeshment) (Benschoten *et al.* 1994; Gregor *et al.* 1997). Following the flocculation and coagulation processes, flocs formed are then removed by means of sedimentation and/or filtration (Faust and Aly 1998; Wang *et al.* 2002).

The optimum conditions for coagulation are usually determined using jar tests. Jar testing includes varying the amount of coagulants and the sequence in which they are added to samples of raw water in jars or beakers. The solution is then stirred so that the formation, development, and settlement of flocs can be observed (Faust and Aly 1998). Through jar testing, coagulation mechanisms as well as coagulation efficiency can be depicted. Coagulation efficiency is commonly expressed as the ratio of supernatant turbidity of the final (coagulated) solution to the initial solution; a ratio of close to zero is desirable as few potential foulants are left in solution.

The coagulation mechanism can be divided into four different zones depending on the 'degree of destabilization' (Dentel 1988), which is influenced by the concentration of coagulant, solution pH and turbidity. These zones include (I) stable suspension, (II) adsorption destabilization, (III) restabilization, and (IV) sweep coagulation (Dentel 1988); particle destabilization occurs in zones II and IV. As shown in Figure 2.9(b), when aluminum salts are used as the coagulant, the degree of destabilization can be

plotted on the aluminum solubility diagram (as shown in Figure 2.9(a)) in order to depict the aluminum species involved in each coagulation zone.

Figure 2.9 Aluminum solubility diagram (a) and alum coagulation diagram (b). Indicated zones in (b) are as follows: I, stable suspension; II, adsorption destabilization; III, restabilization; IV, sweep coagulation, Opt IV, optimum coagulation zone as adopted from (Dentel 1988).

2.4 Hybrid Coagulation-Membrane Filtration Technique

It has been shown that coagulation as a pre-treatment process of membrane filtration could significantly alleviate flux decline compared to that without pre-treatment (Kim *et al.* 2006; Shon *et al.* 2005). Some early studies conducted to investigate the effect of coagulation as a pre-treatment of membrane filtration are as follows:

Shon *et al.* (2005) studied the flocculation of organics as a pre-treatment of UF membranes. They found that foulant concentration on the membrane is lower when flocculation of organics is conducted before the filtration step, thus mitigating membrane fouling. Although some studies have reported that flux improvement was achieved when performing coagulation prior to MF and UF (Jung *et al.* 2006; Kimura *et al.* 2008; Lahoussine-Turcaud and Wiesner 1990), Shon *et al.* (2005) shows that the

improvement was marginal when coagulation was performed as a pre-treatment to NF, whereas a study by Schäfer et al. (2001) shows that coagulation in feed solution as opposed to in the boundary layer did not cause significant flux decline during nanofiltration.

Lee et al. (2000) studied different types of flocs formed on membrane surface when coagulation is performed under different conditions; they found that less compressible flocs are formed via charge neutralization mechanism, whereas more compressible flocs are formed via sweep flocculation. Wang et al. (2002) found similar result and suggested that charge neutralization mechanism dominates at pH 5 while sweep flocculation mechanism plays an important role at pH 7. Gregor et al. (1997) studied the optimum pH for NOM removal by aluminum coagulation, and suggested that initial coagulation pH of 4-5 allows the formation of bridged NOM-aluminum complexes which act as a nuclei for macro-flocs formation.

One interesting study by Lee et al. (2005d) on coagulation of organics in the presence of hematite particles and salts and its behavior upon deposition on MF membranes shows that flocs formed with the order of salt-particle-organics (hematite is initially flocculated in the presence of salts and then contacted with the organics) have a lower specific cake resistance and compressibility compared to that with the order of organics-particle-salts. They further suggested that flocculation prior to membrane filtration should be encouraged as the cake formed would be less robust. Sander et al. (2004) measured the interparticle forces between humic acid and particle surfaces (alumina and hydrous iron oxide) in the presence of calcium ions using the Atomic Force Microscope (AFM) force measurement method. They suggested that the forces acting between the two surfaces include electrostatic forces, steric barrier, van der Waals attraction, and adhesive bridging of humic acid in the presence of calcium ions.

Based on the findings mentioned above and the fact that coagulation pre-treatment is advantageous for improving membrane permeate flux, some studies have looked into combining coagulation and membrane filtration processes. Integrated coagulation-membrane filtration process without an intermediate sedimentation step for solids removal, or the “in-line coagulation”, “in-line flocculation” or “hybrid coagulation-membrane filtration” technique, has been investigated in recent years for its potential

applications in drinking water treatment process (Choi and Dempsey 2004; Erdei *et al.* 2008; Guigui *et al.* 2002; Oh and Lee 2005). This technology offers advantages such as reduction of coagulant dose, mixing-time, energy consumption and head loss (Oh and Lee 2005), and has been shown to effectively remove NOM while maintaining high flux recovery (Guigui *et al.* 2002; Kim *et al.* 2006). However, none has attempted to systematically investigate the performance of this technique for organics removal when calcium ions are present and their subsequent fouling mechanisms in these systems, and to delineate the interactions between NOM and calcium ions in the presence of coagulant. In addition, on top of removing organics while maintaining high permeate flux, the added value of hybrid coagulation-nanofiltration technique such as removal of disinfection by products (DBPs) has not been systematically studied.

2.5 Summary

Nanofiltration has been employed in drinking water treatment and wastewater reclamation as it is capable of removing impurities down to the size of divalent ions. This technique, like other membrane filtration techniques, suffers from fouling which could be promoted by various factors (feed water composition, membrane properties and operational conditions). One of the commonly found foulants in raw water and secondary wastewater effluent is NOM, which is considered as a major foulant due to its ubiquitous and recalcitrant properties. In the presence of both NOM and calcium ions, fouling was found to be more severe as a result of cross-linked organic fouling layer. In drinking water treatment, NOM is commonly removed by coagulation. Some studies suggested that integrating coagulation and membrane filtration could be beneficial in removing NOM, reducing the coagulant requirement and energy consumption, as well as maintaining high permeate flux.

Chapter 3

Materials and Methods

3.1 Materials

3.1.1 Membranes

Two types of NF membranes (NF-270 and NF-90, supplied by Dow FilmTec) were used in this study. NF-270 is a piperazine based semi-aromatic polyamide thin-film composite (TFC) membrane made from piperazine and benzenetricarbonyl trichloride, whereas 1,3-phenylene diamine is used instead of piperazine in NF-90 (Boussu *et al.* 2006). As summarized in Table 3.1, NF-270 is looser compared to NF-90 with a smooth membrane surface, and consequently its pure water flux is higher (Tang *et al.* 2007c). NaCl rejection in NF-90 is higher compared to NF-270 due to its smaller pore size, which makes it a good option for rejecting ions such as bromate. As shown by the contact angle and zeta potential values, NF-270 is more hydrophilic and more negatively charged and therefore less susceptible to fouling. Figure 3.1 shows the SEM images of NF-270 and NF-90 membranes.

Membrane provided by the suppliers came in dry rolled sheets and was stored at 4°C in the dark. 48 hours prior to filtration experiment, membrane sheet was cut into smaller sheets (14.5 × 9.7 cm for cross-flow nanofiltration experiments, and 47 mm diameter for dead-end experiments), soaked in DI water and kept at 4 °C.

NF-270 was used in all of filtration and fouling experiments, while NF-90 was used specifically to investigate the removal of bromate/bromide ions.

Table 3.1 Properties of nanofiltration membranes used in this study (Boussu *et al.* 2006; Manttari *et al.* 2004; Tang *et al.* 2007c).

Membrane	Molecular weight cut-off (Da)	NaCl ^a rejection (%)	Contact angle (°)	Zeta potential (mV) ^b			Roughness (Å)
				pH 3	pH 4.5	pH 7	
NF-270	155	59	27	2.4	-12.1	-32.6	46
NF-90	100	92	54	3.7	17.5	-26.5	388

^a Rejection experiments were conducted using cross-flow setup at a cross-flow velocity of 450 cm/s at a TMP of 8 Bar (116 psi) as stated in (Boussu *et al.* 2006).

^b Zeta potential values were taken from (Tang *et al.* 2007c) except for NF-90 at pH 3 which was taken from (Boussu *et al.* 2006).

Figure 3.1 SEM images of virgin membranes at 20 kV voltage. Image on the left is NF-270 and on the right is NF-90.

3.1.2 NOM

Humic acid

Humic acid was obtained from Sigma-Aldrich (St. Louis, USA). The reported molecular weight for Aldrich humic acid (AHA) ranges from 3000 to 23,000. In order to remove the fulvic, metal and ash content, AHA was pretreated with a method adopted from the International Humic Substances Society (IHSS) (Swift 1996). The

pre-treatment steps are as follows: AHA was acidified with 1 M HCl to give a final concentration of 0.1 g dry AHA/mL solution and a final pH of 1. Next, the suspension was shaken for 1 hour and centrifuged at 3,300 rpm for 15 minutes. Using decantation, the supernatant was separated from the residue. Sodium hydroxide was added to the residue to give a concentration of 0.1 g dry HA/mL of solution at pH 13. The mixture was then shaken for at least 4 hours, and was allowed to settle overnight. Centrifugation and decantation were carried to separate the supernatant and residue, but at this stage the supernatant was collected.

The supernatant was then filtered twice through a 0.2 μm polyethersulfone (PES) filter and the filtrate was acidified to pH 1 with 6 N HCl. After overnight settling, centrifugation and decantation were performed one more time in order to obtain the residue. This residue was then transferred to a 3,000 Da membrane dialysis tube, and the solution was dialyzed in a large DI water bath. The DI water was changed hourly in the first day and daily for the next 10 consecutive days to allow dialysis to occur. Dialysis was stopped when the conductivity of the dialyzing water was less than 8 $\mu\text{S}/\text{cm}$. Pretreated Aldrich humic acid (PAHA) was then freeze dried for 5 days and stored in the dark at 4 $^{\circ}\text{C}$.

Alginate

Sodium alginate from brown algae was obtained from Sigma-Aldrich (St. Louis, USA). As specified by the manufacturer, the molecular weight for Aldrich sodium alginate ranges between 80,000 to 120,000 Da. Stock solution of 3 g/L sodium alginate was prepared for filtration experiments. This solution was filtered through 0.45 μm Nylon filter to remove impurities. Nylon filter was changed every 30 minutes to ensure that sodium alginate was not removed significantly by the filter. The resulting filtered stock solution was kept at 4 $^{\circ}\text{C}$ and discarded after 2 weeks.

3.1.3 Other chemicals

All chemicals used in this study are analytical grade except for humic acid (technical grade) and used without further pre-treatment, unless stated otherwise. Deionized water (Elga, LabWater, UK) was used to prepare the chemical and feed solutions,

which were stored at 4 °C. All of the chemicals used in the experiments are listed in Table 3.2.

Table 3.2 List of chemicals used in this study.

Chemical name	Purpose of use	Manufacturer	Remarks
Sodium chloride, NaCl	Background electrolyte	Fisher Scientific	Added in powder form
Calcium chloride, CaCl ₂	Foulant	Fisher Scientific	3 M stock solution
Hydrochloric acid, HCl	pH adjustment	Fisher Scientific	0.1 N solution
Sodium hydroxide, NaOH	pH adjustment	Fisher Scientific	0.1 N and 0.01 N solutions
Alum salts, Al ₂ (SO ₄) ₃ .14-18H ₂ O	Coagulant	Fisher Scientific	10 g/L stock solution
Sodium alginate	Foulant	Sigma-Aldrich	Pretreated, refer to Section 3.1.2
Humic acid	Foulant	Sigma-Aldrich	Pretreated, refer to Section 3.1.2
Sodium azide, NaN ₃	Anti-biofouling	Fisher Scientific	Added in powder form
Sodium Bromate, NaBrO ₃	Rejection experiment	Fisher Scientific	4 mM stock solution
Sodium Bromide, NaBr	Rejection experiment	Sigma-Aldrich	10 mM stock solution
Ferrous sulphate, FeSO ₄	Coagulant	Sigma-Aldrich	Added in powder form
Sodium hypochlorite, NaOCl	Extractant	Sigma-Aldrich	400 mg/L concentration

3.2 Methods

3.2.1 Jar test

Jar tests were conducted to evaluate the behavior of NOM (humic acid and alginate) when coagulated with alum or ferrous sulphate. Ferrous sulphate was chosen due to its reducing capability (in this study, it was used to reduce bromate to bromide – refer to Chapter 7) and it will eventually precipitate in the form of $\text{Fe}(\text{OH})_3$, which functions as a coagulating agent. Floc formation and NOM removal were the two investigated parameters. For this purpose, coagulant concentration was varied between 0-150 mg/L while NOM concentration was kept at either 30 or 15 mg/L. The ionic strength and pH for all systems were adjusted to 10 mM as NaCl and 7 ± 0.1 , respectively. In Chapters 4 to 6, fouling of different combinations of NOM, alum coagulant and calcium chloride were investigated, while in Chapter 7 the coagulation of humic acid by ferrous sulphate was studied. All of the feed solutions were prepared following the protocol below:

Preparation of the feed solution

Preparation of feed solution is divided into three different groups: preparation for system containing NOM-coagulant (System 1), preparation for system containing NOM-calcium-coagulant (System 2), and preparation for system containing NOM-calcium (System 3), as shown schematically in Figure 3.2:

System 1: Alum and NOM (humic acid or alginate) were added simultaneously to DI water and the volume was adjusted to 300 mL. This was followed by rapid mixing (250 rpm) for 5 minutes while pH was adjusted to 7 ± 0.1 by adding base, and the ionic strength was adjusted to 10 mM as NaCl. Slow mixing at 50 rpm for 30 minutes was then conducted to allow flocculation.

Figure 3.2 Preparation of the different feed solutions.

System 2: NOM (humic acid or alginate) and CaCl₂ were added simultaneously to DI water and the volume was adjusted to 300 mL. This was then followed by rapid mixing (250 rpm) for 5 minutes. Alum is then added into the system, followed by rapid mixing (250 rpm) for another 5 minutes while adjusting the pH to 7 ± 0.1 by means of acid/base addition, and the ionic strength was adjusted to 10 mM as NaCl. This is then followed by slow mixing (50 rpm) for 30 minutes to allow flocculation.

System 3: NOM (humic acid or alginate) and CaCl₂ are added simultaneously to DI water and the volume was adjusted to 300 mL. This was then followed by rapid mixing (250 rpm) for 5 minutes while adjusting pH the pH to 7 ± 0.1 by means of acid/base addition, and the ionic strength was adjusted to 10 mM as NaCl.

3.2.2 Filtration experiments

Filtration experiments were conducted using dead-end and cross-flow configurations. Dead-end nanofiltration setup was used in alginate and humic acid fouling experiments (refer to Chapter 4 and 5) and bromate rejection experiment (refer to Chapter 7), whereas cross-flow nanofiltration setup was used only in alginate fouling experiment (refer to Chapter 6). Experimental protocol for fouling experiments

consists of 3 steps: (1) membrane compaction with DI water, (2) conditioning with background electrolyte (10 mM NaCl at pH 7), and (3) fouling test. The length of these steps depends on the nanofiltration configuration. In summary, the experimental protocol is shown in Table 3.3.

Table 3.3 Experimental protocol for fouling experiments in dead-end and cross-flow configurations.

Steps	Length (h)	
	Dead-end configuration	Cross-flow configuration
Membrane compaction with DI water	2	48
Conditioning with electrolyte solution	2	24
Fouling test	16, or until all feed is filtered	30

Clean water flux is defined as the permeate flux measured at the end of membrane compaction period (2 hours for dead-end configuration and 48 hours for cross-flow configuration). After this period, 10 mM of NaCl was added into the feed tank and conditioning was conducted for a certain period of time (2 and 24 hours for dead-end and cross-flow, respectively). Salt rejection was determined at the end of this period by measuring the conductivity of permeate. Calibration curve for determining the concentration of NaCl is shown in Figure A.1 of the appendix.

Dead-end nanofiltration setup

Dead-end nanofiltration setup used in this study is schematically shown in Figure 3.3. This setup comprises of a nitrogen gas tank, 800 mL reservoir tank (Millipore Corporation, Bedford, USA), 50 mL stainless steel stirred cell (Millipore Corporation, Bedford, USA) and a weighing scale connected to a data logger. The stirred cell

houses a 47 mm diameter flat membrane sheet with an effective area of 14.5 cm². Pressure in the feed tank was provided by the nitrogen gas. Permeate samples were collected in a glass beaker covered with Parafilm, and the mass was measured continuously. Data of permeate mass and pressure were collected every minute and the results were stored in a computer.

Figure 3.3 Schematic diagram of the bench-scale dead-end nanofiltration test setup.

Cross-flow nanofiltration setup

The cross-flow nanofiltration setup consists of two 40 L feed tanks and two membrane testing cells configured in parallel (SEPA CF II, GE Osmonics, Minnetonka, MN) as shown in Figure 3.4. Feed solution was pumped into the membrane cells by a diaphragm pump (Hydra-Cell, Wanner Engineering, Minneapolis, MN). Backpressure relieve valve and a by-pass line were placed prior to the pump as a safety measure. The pump pressure was controlled using an inverter (Emerson, Emerson Process Management Asia Pacific Pte Ltd, Singapore) to produce 5 L/min feed flow rate (to provide both membrane cells, at 2.5 L/min for each cell) at 23 ± 0.5 Bar (2,300 kPa). Feed temperature in Tank 1 was maintained at 25 ± 0.5 °C using a re-circulating water chiller, at a temperature of 15 °C. Solution pH in Tank 1 was maintained at 7 ± 0.5 using 0.1 M HCl and 0.1 M NaOH, which were pumped automatically as soon as the pH was out of the range. Tank 1 was equipped with a mechanical stirrer (Cole-Palmer, Vernon Hills, IL).

Feed solution was pumped from Tank 1 and the flow was divided equally into both membrane cells. Cross-flow velocity for each membrane cell was maintained at 15.5 cm/s (at 2.5 L/min of feed flow rate) using a needle valve (Swagelok, Sunnyvale, CA) at the inlet of the cell. The retentate flowed through a pressure gauge (Span, Waukesha, WI) and flow meter (Cole-Palmer, Vernon Hills, IL), and eventually back into the feed tank to maintain the feed concentration. Permeate flow was monitored using a digital flow meter. Both permeate flows were recycled separately back into the feed tank where manual sampling/measurement using a graduated cylinder and stop watch was conducted. A control panel with an industrial personal computer was used for displaying pressures (feed, membrane cell A, membrane cell B), temperatures (feed tank and water chiller), pH, and flow rates (feed, retentate, permeate from each cell) and to automatically control the temperature and pH of the feed solution.

Each membrane cell houses a 14.5×9.7 cm membrane sheet. The channel height is 4 mm. After the membrane sheet, feed spacer and permeate carrier were loaded into the cell, the channel height was 2.8 mm. The cell holder must be pressurized prior to filtration experiment. In order to pressurize the cell holder, a hand pump (SPX Power Team, Rockford, IL) was connected to both cell holders to provide a pressure of 500 psi (3,450 kPa).

Figure 3.4 Schematic diagram of the cross-flow nanofiltration setup.

3.2.3 Humic acid extraction

Humic materials accumulated on membrane were extracted with sodium hydroxide following the method reported in (Tang *et al.* 2007b). First, fouled membrane coupon was gently washed with DI water to remove labile humic material. Then, sodium hydroxide (NaOH) as an extractant (0.1 N, 50 mL) was added to the cell and stirred at 250 rpm for 1 hour. Humic acid concentration in the extract was then measured using a UV/vis spectrophotometer (Shimadzu UV-1700, Kyoto) using quartz sample tube with a path length of 1 cm at a wavelength of 254 nm. Calibration curve was constructed for humic concentrations between 1 to 15 mg/L, with R^2 values better than 0.99. It was found in the pre-test that a second extraction with 0.1 N NaOH following this method would only contribute an additional 1% of the extracted humic materials, hence one-step extractions were performed for the whole experiments.

3.2.4 Alginate extraction

In order to measure the amount of sodium alginate on the membrane after conducting fouling experiment, alginate extraction was performed. Some studies performed alginate extraction using sodium hypochlorite (NaOCl) at concentrations of 120-1000 mg/L and at a temperature between 40-42 °C (Fukuzaki *et al.* 2007; Ye *et al.* 2005). In this study, the extraction method was further developed to find the optimum condition of extraction, namely the concentration of sodium hypochlorite, temperature and duration that gives the highest extraction efficiency.

For this purpose, a set of membrane sheets (47 mm diameter) was fouled with 30 mg/L of alginate prior to extraction. Each fouled membrane sheet was soaked in 50 mL sodium hypochlorite solution and heated to a certain temperature in a water bath. Extraction was performed for 2-8 hours. Sodium hypochlorite concentration was varied between 100 to 500 mg/L, and the extraction temperature was varied at 42 and 45 °C. As seen in Table 3.4, the efficiency of extraction increases with increasing sodium hypochlorite concentration, temperature and duration of extraction. It was found that when the extraction was performed for more than 6 hours, evaporation of solution occurred. The highest efficiency was reached at 400 mg/L and 500 mg/L of

sodium hypochlorite at 45 °C and 6 hours of extraction with a discrepancy of less than 10%. Hence, in this study, all alginate extraction was performed at 400 mg/L sodium hypochlorite, at 45 °C for 6 hours.

Table 3.4 Efficiency of sodium alginate extraction using sodium hypochlorite at various conditions.

No.	NaOCl conc. mg/L	Temperature (°C)	Duration (h)	Cake mass (mg)		Efficiency (%)
				Formed	Desorbed	
1	100	42	2	12.81	9.45	74
2	200	42	2	12.43	9.32	75
3	250	42	2	11.91	9.44	79
4	300	45	2	12.32	9.89	80
5	350	45	2	12.53	10.35	83
6	400	45	2	12.21	10.43	85
7	400	45	4	12.23	10.85	89
8	400	45	6	12.9	11.76	91
9	400	45	8	11.98	evaporated	-
10	500	45	2	12.02	10.36	86
11	500	45	4	12.12	10.81	89
12	500	45	6	12.3	11.24	91
13	500	45	8	12.43	evaporated	-

Sodium alginate concentration in the extract solution was then measured using TOC analyzer ((Shimadzu TOC-VCSH, Shimadzu Scientific Instruments, USA). Standard solutions of sodium alginate in 400 mg/L sodium hypochlorite were prepared to construct the calibration curve with R^2 values better than 0.95.

For samples containing sodium alginate and calcium, sodium hypochlorite method could not be used to extract alginate. In this case, the calcium alginate extraction method as adopted from (Qiu *et al.* 1996) was performed. The first step of this method is soaking the fouled membrane coupons in 0.5 M HCl for 30 minutes to convert calcium alginate into alginic acid, following the reaction:

The addition of HCl will result in precipitation of alginic acid film, which can be easily separated from the membrane. This film is then carefully transferred to another beaker and an excess amount of NaOH was added. This step transforms the alginic acid back into sodium alginate. The concentration of sodium alginate can be measured using a TOC analyzer, with standard solutions containing sodium alginate in NaOH solution.

3.2.5 Analytical methods

Alginate concentration

Concentration of sodium alginate in the feed solution, permeate and extracted from the fouled membrane was measured using a total organic carbon analyzer (Shimadzu TOC-VCSH, Shimadzu Scientific Instruments, USA). Calibration standards with at least 8 points with triplicate standards for each point were prepared for each measurement, as shown in Figure A.2 of the appendix. Calibration curves with R^2 values larger than 0.95 were constructed for each system, which includes alginate, alginate and calcium, alginate and alum, alginate, calcium and alum, to correct any interference in the measurements. Calibration standards of sodium alginate in 400 mg/L NaOCl solution were prepared for measurements of extracted alginate and to construct the calibration curve.

Humic acid concentration

UV-vis spectrophotometer (Shimadzu, UV-1700, Japan) was used to measure humic acid concentration in the feed solution, permeate and extracted from the fouled membrane. A quartz sample cuvette with a path length of 1 cm was used. Measurements were conducted at a wavelength of 254 nm, at which maximum absorbance was observed. Calibration curves with R^2 values larger than 0.99 were constructed for humic concentrations ranging between 1 to 100 mg/L, as shown in Figure 3.5 and for concentrations ranging between 1 to 15 mg/L, as shown in Figure A.3 of the appendix. The calibration curve consisted of 9 points, with triplicate standards measured for each point. Calibration curve for humic extracted from

membrane was prepared in 0.1 N NaOH background solutions with humic concentrations ranging between 1 to 15 mg/L (Figure 3.6).

Figure 3.5 Humic acid calibration curve at $\lambda = 254$ nm for measurements of PAHA concentrations in feed solution. DI water was used as the background solutions.

Figure 3.6 Humic acid calibration curve at $\lambda = 254$ nm for measurements of PAHA concentrations in extract solution. 0.1 N NaOH was used as the background solutions.

Sodium, aluminum, calcium, and iron concentrations

Inductively coupled plasma with optical emission spectrophotometry (ICP-OES) with auto-sampler (Optima 2000 DV, PerkinElmer Optima, Waltham, MA) was used to measure the sodium, calcium, aluminum and iron concentrations in the feed and permeate solutions. This instrument has a detection limit of 0.005, 0.001, 0.002, and 0.001 mg/L for sodium, calcium, aluminum and iron concentrations, respectively. Each sample was measured in at least three replicates, and the reported values were the averages of the replicates.

Bromate and bromide concentrations

Bromate and bromide concentrations in the feed and permeate solutions were measured using an ion chromatography (IC) with 38 mM sodium hydroxide (NaOH) eluent (Dionex ICS-1000, Dionex Corporation, Sunnyvale, CA) and an IonPac AS15 analytical (4 × 250 mm) column (Dionex ICS-1000, Dionex Corporation, Sunnyvale, CA). This instrument is equipped with an auto-sampler and a reagent-free controller unit (both units are also from Dionex). Flow rate of the eluent was 1.2 mL/min with a sample injection volume of 25 μ L. Standard solutions containing equal ratio of bromate to bromide at concentrations of 1, 5, 10, 15 and 20 mg/L were prepared for each measurement. Minimum detection limit for both bromide and bromate is 1 mg/L.

Zeta potential

Zeta potential values of foulants were measured using a zeta potential analyzer (Zetasizer Nano-ZS, Malvern Instruments, Worcestershire, UK). Samples were injected into clear disposable zeta cells (Malvern Instruments, Worcestershire, UK), which were washed three times with DI water and two times with sample solutions prior to measurements. Five replicates were made for each measurement, and the reported values were the averages of these replicates.

Viscosity

Viscosity measurement was carried out using a rotational viscometer (Rheolab MC1, Anton Paar, Ashland, VA) with a concentric cylinder for measuring low to medium viscous fluids. The shear rate ($\dot{\gamma}$) value was set at 50 s^{-1} for all measurements. DI water viscosity was measured prior to the samples for each measurement, and the

reported viscosity values are normalized by the DI water viscosity. Each sample was measured either in triplicates or quadruplicates, with 50 mL volume of sample used in each measurement.

Particle size

The volumetric size distribution of foulants was measured using laser diffraction technique (Mastersizer 2000, Malvern Instruments, Worchestershire, UK), which could measure particles down to a diameter of 0.02 μm . Samples were measured immediately after being prepared at a stirring speed of 100 rpm, which was the same stirring speed used in the feed tank. Each measurement was conducted in 99 cycles over a span of 30 minutes. Since the sampling pump was activated after 8 minutes of operation at this stirring speed, only the last half of the data (the last 50 cycles) were considered as the results. Results were obtained as volumetric size distribution, and the average particle size was calculated from the particle size diameter corresponding to the 50th percentile, or $d(0.5)$.

Membrane imaging and surface roughness

An AFM (NanoScope III scanning probe microscope, Digital Instruments, Santa Barbara, CA) was used to take images of the membrane surface and to characterize the surface roughness of virgin membranes. Membrane sheets were cut into 0.5 $\times$ 0.5 cm coupons, which were fixed onto sample mounting steel discs. AFM images were obtained in tapping mode, with a resolution of 25 μm^2 .

In addition to AFM, Scanning Electron Microscopy (Zeiss Evo SEM, Carl Zeiss SMT, Germany) was also used to take images of clean and fouled membrane sheets. Membrane samples were dried in the 4 $^{\circ}\text{C}$ fridge, cut to 0.5 $\times$ 0.5 cm coupons, fixed to sample mounting discs using conductive tape and then coated with platinum prior to measurement to increase the conductivity and mechanical stability. Samples were measured at a voltage of 20 kV and magnification up to 10,000.

Chapter 4

Low Molecular Weight NOM: Humic Acid

4.1 Introduction

Nanofiltration (NF) has been gaining attention as the polishing step in water treatment technology. Having characteristics half-way between ultrafiltration (UF) and reverse osmosis (RO), NF offers higher permeate flux compared to that of RO (Tang *et al.* 2007c) and allows rejection of smaller and charged molecules compared to that of UF. Compared to larger pore membranes such as UF and microfiltration (MF), NF membranes suffer little or no pore blocking (Listiarini *et al.* 2008; Sadreddini *et al.* 2008) and hence the resistance due to pore blocking which contributes to the total cake resistance is minimal. Some researchers investigated the rejection abilities of NF towards trace organic and inorganic contaminants (Steinle-Darling and Reinhard 2008; Wu and Sun 2005; Wu *et al.* 2004a). These advantages have accelerated the use of NF technologies in drinking water treatment and wastewater effluents reclamation as an alternative for RO and UF. One major challenge in NF technology is membrane fouling. At constant applied pressure, fouling causes a decline in permeate flux over time. Although periodic membrane cleaning will restore the permeate flux, membrane replacement will eventually be inevitable, resulting in higher operational and maintenance costs.

Foulants can be categorized into several groups such as sparingly soluble (inorganic) salts, organic substances, colloidal and particulate matter and biological growth. NOM such as humic acid is considered to be one of the major causes of membrane fouling. Numerous studies have reported the physical and chemical aspects of fouling of NF by humic acid (Amy and Cho 1999; Cho *et al.* 1999; Cho *et al.* 1998; Hong and Elimelech 1997; Li and Elimelech 2006; Schafer *et al.* 1998; Tang *et al.* 2007a). Tang *et al.* (2007b) reported that humic acid fouling of NF and RO membranes was a function of initial flux and feed water composition, and that the flux decline was likely more dependent on the foulant-deposited foulant interaction rather than on the virgin membrane properties.

In drinking water treatment train, NOM is commonly removed via coagulation/flocculation using coagulating agents such as aluminum. When coagulation is performed together with membrane filtration (hybrid coagulation-filtration), organic matter can be removed effectively while high flux recovery is maintained (Lee *et al.* 2000; Shon *et al.* 2005). Although hybrid coagulation-microfiltration and -ultrafiltration have been proposed by some researchers (Jung *et al.* 2006; Kimura *et al.* 2008; Lahoussine-Turcaud and Wiesner 1990; Seockheon *et al.* 2006), it was shown that flocs and uncoagulated humics with sizes smaller or similar to membrane pores may cause irreversible fouling (Kimura *et al.* 2008). In addition to this, hybrid coagulation-filtration for these membranes only marginally improves permeate flux in some cases and results in considerable amount of coagulant in permeate due to low rejection (Jung *et al.* 2006; Lahoussine-Turcaud and Wiesner 1990). These results give insights to the possibilities of employing hybrid coagulation-nanofiltration technology in removing organic matter since pore blocking in NF membranes is negligible, and NF membranes give higher rejection compared to MF and UF membranes.

In addition, divalent cations such as calcium and magnesium that are naturally present in raw waters may complicate the system even further. These ions which have a strong potential to form complexes with NOM are capable of forming bridges between membrane surface and NOM (Lee and Elimelech 2006; Li and Elimelech 2004; Tang *et al.* 2007b). A number of studies have been conducted to investigate the effect of divalent cations on NOM fouling of various membranes (Childress and

Elimelech 1996; Lee *et al.* 2005b; Li and Elimelech 2004, 2006; Seidel and Elimelech 2002; Tang *et al.* 2007b; Zhu and Elimelech 1997), and found that more severe flux declines occurred in these systems. While these studies give insights on the foulant-foulant and foulant-membrane interactions when calcium ions are present in the system, these interactions might behave differently when coagulant pre-treatment is conducted.

The objectives of this study are to systematically investigate the flux decline trends in systems containing humic acid, calcium ions, aluminum-based coagulant and their combinations, and subsequently evaluate the cake compressibility and fouling mechanism of these systems based on the findings. In this study, a dead-end bench-scale nanofiltration membrane system was used and resistance calculation was performed to assess the foulant-foulant and foulant-membrane attachments. Permeate quality in each system was analyzed to determine humic acid and divalent cations removal. Other characterization methods such as jar tests and laser diffraction techniques were performed.

4.2 Experimental Section

4.2.1 Materials

Chemicals

Unless stated otherwise, all chemicals were analytical grade. Chemical and feed solutions were prepared with deionized (DI) water (Elga LabWater, UK) with a resistivity of 18.2 M Ω cm. Sodium hydroxide and hydrochloric acid were diluted from 1 N volumetric standard; 6 N hydrochloric acid was diluted from concentrated hydrochloric acid (34-37% HCl, trace metal grade, Fischer Scientific, Pittsburg, PA). Reagent grade alum salts ($\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$) and calcium chloride (Fisher Scientific, Pittsburg, PA) were used as the model coagulant and calcium ions respectively.

Purified Aldrich humic acid (PAHA)

AHA (Sigma-Aldrich, H16752, technical grade, St. Louis, MO) was pre-treated following the method described in (Tang *et al.* 2007a) and as described in Section 3.1.2 in order to remove fulvic, metal and ash contents. Stock solutions of 3 g/L were prepared from the freeze-dried PAHA, stored in the dark at 4 °C, and discarded after 3 months. Feed solutions for fouling experiments were prepared from the stock solution.

NF membranes

All experiments were performed with NF-270 membrane (Dow/FilmTec, Minneapolis, MN). This polyamide thin-film composite membrane is considered as smooth membrane with a reported average roughness of 9.0 ± 4.2 nm (Tang *et al.* 2007b). The average hydraulic resistance of the membrane was determined to be $2.46 (\pm 0.2) \times 10^{13} \text{ m}^{-1}$ (measured with DI water at 25 ± 1.0 °C). The range of pH for this membrane for continuous operation as specified by manufacturers is 3-10. Other properties of this membrane are 43% NaCl transmission (Steinle-Darling and Reinhard 2008) determined at 80 psi (550 kPa), 40-60% CaCl_2 and <3% MgSO_4 transmissions (given by manufacturers).

4.2.2 Bench-scale dead-end nanofiltration setup

Fouling experiments were conducted in a bench-scale dead-end nanofiltration system as shown in Figure 3.3. The effective membrane area was 13.4 cm^2 . Permeate flux was collected and the mass was monitored continuously over time using a weighing scale connected to a data logger. Data was collected per second and averaged per minute.

Membranes were soaked in DI water at least for 24 hours prior to fouling experiments. Before each test, membrane inside the cell was compacted with DI water for at least 2 hours, followed by conditioning with background electrolyte (10 mM NaCl at pH 7) for at least 3 hours. Feed solutions were prepared following the protocols in Section 3.3.1. Fouling experiments were conducted for 16 hours or stopped when it had filtered 450 ± 100 mL of feed solution. Attached humic materials on the membrane

surface were extracted and analyzed at the end of each fouling experiment as described in Section 3.3.3.

4.2.3 Methods

Jar tests

Jar tests were conducted to investigate the effects of coagulant concentrations, calcium and settling on PAHA removal. Alum coagulant doses were varied from 0-100 mg/L. Coagulation followed by subsequent flocculation was performed as follows: PAHA and calcium (if needed) were added simultaneously and mixed at 250 rpm for 30 minutes. Alum was then added while the solution pH and ionic strength were adjusted to 7 and 10 mM as NaCl respectively during rapid mixing. Lastly, slow mixing was carried out at 50 rpm for 20 minutes and settling (if needed) for 100 minutes.

Characterization of foulants and membranes

Zeta (ζ) potential values of foulants were measured using a ζ potential analyzer (Zetasizer Nano-ZS, Malvern Instruments, Worcestershire, UK). Reported values are averaged values of five replicates.

The volumetric size distribution of foulants was measured using laser diffraction (Mastersizer 2000, Malvern Instruments, Worcestershire, UK). Samples were measured immediately after flocculation at a stirring speed of 100 rpm, which was the same stirring speed used in the feed tank. Each measurement was conducted for 99 cycles over a span of 30 minutes. Aluminum and calcium concentrations in the feed, permeate, and on the membrane surface were measured using an ICP-OES (Perkin Elmer Optima, Waltham, MA).

The surface roughness of virgin membranes was characterized by AFM (NanoScope III scanning probe microscope, Digital Instruments, Santa Barbara, CA), and AFM images of virgin membranes were obtained in tapping mode with a resolution of $25\mu\text{m}^2$.

Humic acid accumulation

Please refer to Section 3.2.2.

Resistances calculation

Cake resistance, R_c , was determined by applying the Resistances-in-series model. In the first step, DI water was filtered through a virgin membrane to obtain hydraulic membrane resistance, R_m . Next, feed solution containing foulant was filtered through the same membrane coupon to obtain total resistance, R_t . We have found that for the membranes used in this study, the adsorption resistance, R_a , and resistance due to pore blocking, R_p , are negligible compared to the cake resistance. Thus, we may determine the cake resistance by subtracting the total resistance with the hydraulic membrane resistance ($R_t - R_m$).

Empirical specific cake resistance, α_{emp} , was calculated by dividing the cake resistance, R_c , with the accumulated mass on membrane normalized by the effective membrane area (M/A) as stated in Eq. (2.5). Experimental specific cake resistance, α_{MFI} , was estimated using Eqs. (2.4 and 2.6). For this purpose, a plot of t/V versus V was constructed and linear regression was performed. To ensure that the linear regression results in R^2 values larger than 0.95, only the straight portion of the plot was included in the regression. This region is the non-compressible region of the t/V vs. V plot where the MFI equation holds. The slope of the regression equation was used to calculate I by following Eq. (2.4), and subsequently to calculate α_{MFI} by following Eq. (2.6).

4.3 Results and Discussion

4.3.1 Flux performance and permeate quality

Figure 4.1 shows the flux performance of the four investigated systems: PAHA, PAHA and calcium, PAHA and alum, and all three components (PAHA, calcium, alum). Fouling experiments were conducted for at least 16 hours, with filtered volumes of 450 ± 100 mL. As shown in this figure, the least flux decline occurs in

system containing PAHA, calcium, alum. The severity increases in the following order: (PAHA, calcium, alum) < (PAHA, alum) < PAHA < (PAHA, calcium), which implies that the addition of alum coagulant will alleviate flux decline despite the presence of calcium.

Figure 4.1. Permeate flux as a function of time of the investigated systems: PAHA = only humic acid; PAHA+Al = humic acid and alum; PAHA+Ca = humic acid and calcium; PAHA+Ca+Al = humic acid contacted with calcium, then coagulated with alum. Concentrations of humic acid, calcium and alum are 30 mg/L, 1 mM and 30 mg/L respectively. Other test conditions: 25 °C, ionic strength 10 mM NaCl, and pH 7.

Measurements of floc size in these systems as reported in (Listiarini *et al.* 2008) show that alum coagulant is able to form flocs with 2-3 orders of magnitude larger a diameter than the size of PAHA (which is about 0.1 µm). In the case of PAHA and calcium, the measured floc size ranges between 0.1 to 200 µm, which suggests that calcium forms bonds between PAHA molecules to form larger molecules, whose diameter is comparable to those formed when alum is added to PAHA. However, the severity of flux decline in system containing PAHA and calcium indicates that the conformation of each PAHA molecule is more coiled, resulting in more compact fouling layer. The coiled conformation of humic acid in the presence of calcium will be discussed in more detail in the next section.

When all three components are present (PAHA, calcium, alum), the averaged floc size is 1,000 μm and the distribution curve becomes monomodal as compared to bimodal and multimodal in (PAHA + alum) system and (PAHA + calcium) system, respectively (Listiarini *et al.* 2008). This larger averaged floc size could also explain the less severe flux decline in the (PAHA + calcium + alum) system as compared to (PAHA + alum). According to Eq. (2.6), the specific cake resistance is inversely proportional to the squared floc diameter; hence larger flocs will give smaller specific cake resistance, which contributes to larger permeate flux. Furthermore, all of these imply that calcium is also capable of forming bonds between alum-coagulated humic flocs.

Figure 4.2 Permeate quality of NF-270 membranes fouled with solutions containing 30 mg/L PAHA, 1 mM CaCl_2 , and 30 mg/L alum. Other experimental conditions: TMP = 3.5 Bar, ionic strength is 10 mM as NaCl and pH = 7. Error bars indicate the range of data points (experiments were conducted in triplicates for the first three systems and in quadruplets for PAHA).

Figure 4.2 shows the permeate quality of NF-270 membranes during filtration of the investigated systems. Our pre-test has shown that the presence of alum and/or calcium will not affect the UV/Vis reading when measuring PAHA concentration at 254 nm. As seen in this figure, 82% of PAHA is rejected when calcium and/or alum are absent. The addition of calcium and/or alum will improve PAHA removal to greater than

98% due to the larger floc size as discussed earlier. Another possible explanation for the improved PAHA rejection is that by visual observation the fouling layer for the three systems (when calcium and/or alum are added) is cohesively bounded, whereas when only PAHA is present the fouling layer is not cohesively bounded. This bounded layer might act as an additional filter for the PAHA molecules, hence improving the rejection.

4.3.2 Membrane fouling index (MFI) curve

After observing the flux performances in the previous section, resistance calculations and analyses were performed to further understand the cake compressibility and fouling mechanisms in the investigated systems. A plot of ratio of filtration time and filtrate volume (t/V) as a function of total filtration volume (V) was constructed for each system as shown in Figures 4.3(a-d). In general, NF-270 membrane suffers little pore blocking as shown by the initial sharp increase of the curve. This is justified by our findings that the resistances due to pore blocking and adsorption are negligible compared to the membrane resistance. In system containing only PAHA (Figure 4.3(a)), the region of cake formation without compression is clearly defined, as shown by the straight line after about 20 mL of filtration. However, this is not followed by the third region which is the cake formation with compression region. This suggests that the fouling layer formed by PAHA is slightly- if not non-compressible.

When calcium is present, as shown in Figure 4.3(b), the non-compressible region is short and immediately followed by a wide region of compressible cake at around 100 mL of filtered volume, suggesting that after a period of filtration time the cake becomes compressible. It is possible that due to the coiled conformation of humic acid in the presence of calcium, the accumulated humic is capable of rearranging or packing itself to form a more compact and dense fouling layer after a certain period of time. This is shown by the less-sharp initial flux decline (Figure 4.1) during the first 100 minutes (which corresponds to 100 mL of filtered volume), but unlike the systems where alum are added, it continues to decline throughout the filtration period. This accumulation is also aided by the capability of calcium to form bonds with humic molecules.

Figure 4.3 Ratio of filtration time and filtration volume as a function of total filtrate volume of the investigated systems: (a) PAHA, (b) PAHA and calcium, (c) PAHA and alum, (d) PAHA, calcium, alum. Standard test conditions as in Figure 4.2 were applied.

In the presence of alum (Figures 4.3(c-d)), the plot of t/V over V seems not to have defined second and third regions (cake formation without and with compression, respectively), suggesting that more than one fouling mechanisms occur simultaneously. As shown in the figures, a short region of pore blocking is observed in the initial filtration period. This is then followed by a mixed region of compressible and non-compressible cake formation which is not clearly defined. The last part of the curve seems to be the cake formation without compression, denoted by a straight line. This behavior is observed in both systems where calcium is either present or absent. Similar observation was reported by Katsoufidou et al. (2007a) when investigating fouling of ultrafiltration membrane by sodium alginate.

Figure 4.4 Comparison of specific cake resistance values obtained from experimental (MFI) and empirical methods of the following systems: (a) PAHA, calcium, alum and their combinations: PAHA = only humic acid; PAHA+Al = humic acid and alum; PAHA+Ca = humic acid and calcium; PAHA+Ca+Al = humic acid contacted with calcium, then coagulated with alum; (b) 30 mg/L PAHA and varying alum concentrations between 0 to 100 mg/L. Standard test conditions as in Figure 4.1 were applied, unless stated otherwise.

4.3.3 Specific cake resistance

Specific cake resistance was calculated based on two methods: experimental (MFI) and empirical as explained in Section 4.2.4, and both results were compared in order to observe whether there existed a significant difference between the two methods. Figure 4.4(a) and Table 4.1 show the comparison of specific cake resistances calculated using the experimental and empirical methods for the four investigated systems (only PAHA; PAHA and alum; PAHA and calcium; PAHA, calcium, alum). As shown in these figures and table, the experimental specific cake resistance values of the three combined systems (PAHA, calcium, alum; PAHA and alum; PAHA and calcium) are relatively close to the empirical ones, with ratios of experimental (MFI) to empirical values ranging from 0.2 to 0.38. As for the system containing only PAHA, the empirical value is more than 30 times larger than the experimental.

Table 4.1 Specific cake resistance values and humic attachments of the investigated systems. Error values denote one standard deviation for number of data larger than or equal to 30, and denote the range of data for number of data smaller than 30.

System ^a	$\alpha_{MFI} \times 10^{12}$ (m/g)	$\alpha_{emp} \times 10^{12}$ (m/g)	$\alpha_{MFI} / \alpha_{emp}$ (-)	Attachment ^c (%)
PAHA+Al+Ca	0.22 (± 0.001)	1.10 (± 0.0004)	0.20	93
PAHA+Al	0.65 (± 0.003)	1.70 (± 0.0006)	0.38	79
PAHA	5.82 (± 0.02)	186 (± 0.4)	0.03	1
PAHA+Ca	3.35 (± 0.01)	10.6 (± 0.02)	0.32	68
No Alum ^b	5.82 (± 0.02)	186 (± 0.4)	0.03	1
Alum 10	2.62 (± 0.008)	136 (± 0.38)	0.02	1
Alum 20	0.65 (± 0.002)	2.1 (± 0.0002)	0.31	76
Alum 30	0.65 (± 0.003)	1.70 (± 0.0006)	0.38	79
Alum 50	0.27 (± 0.001)	1.99 (± 0.001)	0.13	71
Alum 100	0.19 (± 0.0006)	2.65 (± 0.003)	0.07	74

^a The following concentrations and test conditions were applied: 30 mg/L PAHA, 30 mg/L alum, 1 mM CaCl_2 , 25 °C, 350 kPa (51 psi), 16 hours filtration time, pH 7, ionic strength 10 mM as NaCl.

^b All solutions contain 30 mg/L PAHA. Alum 10-100 indicates the amount of alum added in mg/L. Test conditions are the same as stated in ^a.

^c Attachment was calculated from the ratio between the amount of PAHA accumulated on the membrane surface (after gentle washing to remove labile materials) to the amount of filtered PAHA. Errors are within 10%.

By visual observation, the addition of alum and/or calcium improves the attachment of PAHA on the membrane surface, as will be discussed in the following section. As shown in Table 4.1, the attachment of PAHA when calcium and/or alum are present is at least 68% as opposed to only 1% when only PAHA is present. As seen in Eq. (2.5), the empirical value of the specific cake resistance, α_{emp} , is calculated by dividing the cake resistance with the accumulated mass normalized by the membrane surface area. When less mass is accumulated on the membrane due to low attachment efficiency, the specific cake resistance will be larger than expected (that is, if we calculate the value based on the total mass in the feed).

On the other hand, if we look at the MFI equations (Eqs. (2.5)-(2.6)) and t/V vs. V plot (Figure 2.3), the specific cake resistance, α_{MFI} , is calculated from the fouling

index, I , and the bulk concentration of foulants, C_b . Here, bulk concentration of foulants is defined as the total mass added into the feed. This implies that during the specific cake resistance calculation, only the total mass and not the actual mass attached on the membrane is considered. Therefore, this equation assumes that the total mass added into the feed (as the bulk concentration, C_b) will attach on the membrane surface. These observations give insights to the possibility of a correlation between attachment efficiency and specific cake resistance.

To further observe this behavior, a set of experiments with varying alum concentrations was conducted. The test conditions were similar to the ones in the previous systems, but calcium was not added. The concentration of alum was varied between 0 to 100 mg/L, and a similar approach of analyses was employed to these systems. Figure 4.3(b) and Table 4.1 show the comparison between specific cake resistance values obtained from the two different methods. As seen, both values are relatively close to each other when 20 mg/L or more alum is added with ratios of experimental to empirical values ranging from 0.07-0.38 and PAHA attachment of more than 70%, whereas in first two systems (only PAHA and alum 10 mg/L) the ratios are 0.03 and 0.02 respectively with PAHA attachment of 1%. This similar observation confirms that there exists a correlation, although not linear, between the foulant attachment and the difference between experimental and empirical specific cake resistance values.

With regard to these observations, we propose to include an attachment coefficient in the MFI equation to account for the attachment efficiency in the fouling index, I :

$$I = \alpha \gamma C_b \quad (4.1),$$

where γ is the attachment coefficient and is dimensionless.

This attachment coefficient does not necessarily have the same value as the attachment efficiency, since no linear correlation was observed. It is possibly a function of foulant and membrane characteristics, and has different values for the

different regions of fouling mechanism as shown in Figure 2.3. Hence, we define the three attachment coefficients based on the regions:

γ_{PB} = attachment coefficient during pore blocking (region 1)

γ_C = attachment coefficient during cake formation without compression (region 2)

γ_{CC} = attachment coefficient during cake formation with compression (region 3).

4.3.4 Zeta potential analysis

It has been shown that the addition of alum and/or calcium into the system enhances the attachment of PAHA. Zeta potential measurements of the investigated systems were conducted to further understand this behavior. Figure 4.5 shows the zeta (ζ) potential values of the four systems. At the investigated pH and ionic strength, all systems were negatively charged with system containing only PAHA being the most negatively charged. This could explain the low attachment efficiency of this system. Since the flux decline of this system is the largest, it suggests that during filtration, humic acid is compressed to form a compact fouling layer, but it is not cohesively bounded to the membrane surface. As soon as the TMP is released, this fouling layer is detached and hence the low attachment efficiency.

The addition of calcium or alum to solutions containing humic acid will result in more positive ζ potential values compared to that of only PAHA. In the case where calcium and alum are added together, the ζ potential values of each system are not additives. The addition of only alum will increase the attachment of foulant to the membrane surface similar to that of only calcium, despite the more negative charge. This indicates that in addition to charge screening and complex formation that occur when calcium is present, there exists other mechanism that could promote the attachment in the presence of alum, possibly sweep flocculation. Since the addition of alum lowers the cake resistance whether calcium is present or not, this shows that the cake formed when alum is present is less compact compared to that when only calcium is present.

Figure 4.5. ζ potential values of the investigated systems. Standard test conditions as in Figure 4.2 were applied. Measurements were conducted in 5 replicates and the error bar denotes one standard deviation. ζ potential value of virgin NF-270 membranes was measured under similar conditions as reported in (Tang *et al.* 2007c).

Similar findings were reported by previous studies (Lee *et al.* 2000; Tang *et al.* 2007b). They found that the cake formed when calcium was present seemed to be denser and thicker and resulted in severe fouling, whereas coagulated foulant in dead-end filtration system resulted in higher membrane permeability. These findings confirm that the cake layer formed in the presence of calcium will be more compact, and the addition of alum will result in less compact cake layer.

4.4 Conclusions

The severity of flux decline of dead-end nanofiltration of systems containing humic acid, calcium, alum, and their combinations is in the following order: (PAHA+alum+calcium) < (PAHA+alum) < (PAHA) < (PAHA+calcium), indicating

that alum coagulant improves permeate flux in a system containing humic acid, regardless the presence of calcium. The fouling layer formed in system containing only PAHA is shown to be non-compressible, whereas in system containing PAHA and calcium the fouling layer is compressible and more compact. In the presence of alum, one or more fouling mechanisms occur simultaneously and the resulting cake layer is less compact. Sweep flocculation might also exist in addition to charge screening and complex formation when alum is present, enhancing the foulant attachment.

We have proposed to add an attachment coefficient in the fouling index equation to account for the attachment of foulants on the membrane surface, which could be a function of foulant and membrane characteristics.

Chapter 5

High Molecular Weight NOM: Alginate – Part I

5.1 Introduction

Nanofiltration (NF) technology has a number of advantages to be applied in many aspects of water treatment systems, including in drinking water treatment and wastewater effluents reclamation. Having characteristics of lower operating pressures compared to reverse osmosis (RO) membranes while capable of removing trace organic and inorganic contaminants (Escher *et al.* 2006; Pronk *et al.* 2006; Steinle-Darling *et al.* 2007; Wu and Sun 2005; Wu *et al.* 2004a, b), NF is seen to be a promising technology in direct and indirect drinking water productions with high water quality.

One of the main obstacles of NF technology is membrane fouling. Fouling in general causes deterioration in permeate quality and quantity, and eventually membrane replacement is unavoidable. Organic fouling and biofouling may be found in indirect drinking water production from secondary wastewater effluents. These are caused by organic matter that may come naturally from drinking water source, synthetically from disinfection processes and domestic use, and biomass which produces soluble microbial products (SMP) and extracellular polymeric substances (EPS) (Shon *et al.* 2006). EPS forms a three-dimensional, gel-like, highly-hydrated matrix in which microorganisms are immobilized, and is the key component of a microbial aggregate (Flemming 2003). This substance comprises of macromolecules such as amino-sugars, bacterial flocs, humic, fulvic, and nucleic acids, among which polysaccharides

are the most commonly found substance (Barker and Stuckey 1999; Duncan *et al.* 2000; Manka *et al.* 1974).

Many researchers have used sodium alginate to model polysaccharides in their studies (Ang and Elimelech 2007; deKerchove and Elimelech 2007; Jermann *et al.* 2007; Katsoufidou *et al.* 2007b; Lee *et al.* 2006; Ye *et al.* 2005) since it behaves similarly to EPS during filtration (Lee *et al.* 2006; Ye *et al.* 2005). In the presence of calcium ions, alginate forms a highly organized gel layer with a structure resembling an egg-box (Grant *et al.* 1973), where calcium binds preferentially to the carboxylic functional groups of alginate and form bridges between the molecules. In membrane filtration, the presence of calcium together with alginate results in different outcomes in terms of permeate flux decline. Some studies show that calcium results in more severe permeate flux decline (Ang and Elimelech 2007; deKerchove and Elimelech 2007; Katsoufidou *et al.* 2007b; Lee and Elimelech 2006), whereas another study shows the contrary (Ven *et al.* 2008). Therefore, one of the objectives of this study is to investigate on what causes the discrepancies by conducting alginate filtration under different concentrations of calcium.

NOMs are removed via coagulation/flocculation using coagulants during water treatment or water reclamation process. Aluminum sulfate (alum) is one of the most commonly used coagulants. Coagulation prior to membrane treatment has been found to be advantageous in terms of improving the permeate flux (Lee *et al.* 2000; Li and Elimelech 2004; Shon *et al.* 2005), and thus reducing the size of water treatment plants. Although hybrid technology of coagulation-filtration has been investigated by a number of researchers (Jung *et al.* 2006; Kimura *et al.* 2008; Lahoussine-Turcaud and Wiesner 1990; Seockheon *et al.* 2006), there is still lack of knowledge on the fouling mechanism when all three components of sodium alginate, calcium and alum are present in the system, and on their contribution to the resistances.

This study is aimed to systematically investigate the fouling mechanism and the corresponding resistances (including cake resistance, resistance due to adsorption, and specific cake resistance) during NF of sodium alginate, calcium and alum.

Available tools such as MFI equations and cake compressibility tests were used, and fouling experiments were conducted with different combinations of foulants (sodium alginate, calcium and alum) and at different calcium and alum concentrations, in our approach to decipher the fouling mechanisms. Furthermore, we proposed a schematic fouling model of these systems to achieve a better understanding of the NF fouling phenomena.

5.2 Materials and Methods

5.2.1 Chemicals

Chemical and feed solutions were prepared with deionized (DI) water (Elga LabWater, Marlow, UK) with a resistivity of 18.2 M Ω cm. Solution pH was adjusted using 1 N and 0.01 N sodium hydroxide (NaOH) and 0.1 N hydrochloric acid (HCl), which were diluted from 1 N volumetric standard and 34-37% concentrated solution respectively (Fisher Scientific, Pittsburg, USA). Sodium alginate from brown algae was obtained from Sigma-Aldrich (St. Louis, USA), with a molecular weight specified by the manufacturer in the range of 12-80 kDa. Stock solution containing 3 g/L of sodium alginate in DI water was prepared and filtered through 0.45 μ m nylon filter, then stored at 4°C and discarded after 3 months. Feed solutions for fouling experiments were prepared from the stock solution.

When alum was used, coagulation and flocculation were included in the feed preparation. The protocol was as follows: sodium alginate and calcium (if needed) were added simultaneously and mixed at 250 rpm for 30 min. Alum was then added and the solution pH and ionic strength were adjusted to 7 and 10 mM as NaCl respectively during rapid mixing. Slow mixing was then conducted at 50 rpm for 20 min.

5.2.2 NF membranes and dead-end NF setup

Commercial polyamide thin-film composite NF-270 membrane (Dow/FilmTec, Minneapolis, USA) was used throughout the experiments. The properties of this membrane are described in Section 3.1.1. Membrane samples were stored in DI water at 4°C, and the storage water was changed regularly. Prior to fouling experiments, membrane sheets were soaked in DI water for at least 48 hours.

A bench-scale dead-end NF setup was used in the fouling experiments as shown schematically in Figure 3.3. A detailed description of this setup can be found in Section 3.2.2.

5.2.3 Fouling experiments

For all experiments, feed solution pH was fixed at 7 using HCl and NaOH, and the ionic strength was adjusted to 10 mM using NaCl. Trans-membrane pressure (TMP) was fixed at 3.5 Bar (350 kPa), except for the compressibility test where the TMP was varied. Alginate concentration in the feed solution was 30 mg/L, alum concentration was 30 mg/L, and CaCl₂ concentration was 1 mM. In one set of experiments, CaCl₂ concentration was varied from 0-6 mM, and in another set of experiments, alum concentration was varied from 0-30 mg/L. Feed solutions were prepared at room temperature (25±1 °C) and stirred at 100 rpm in the reservoir tank.

Fouling experiments were conducted in a bench-scale dead-end NF setup, as described in the previous section. Membrane sheets were soaked in DI water for 48 hours prior to experiment. Then, DI water compaction was conducted for 2 hours or until the flux was stable, and at the end of this step the membrane hydraulic resistance (R_m) was determined. Electrolyte conditioning with sodium chloride solution at pH 7 and ionic strength of 10 mM was conducted for 2 hours following this step. Feed solution was added into the reservoir tank in the last step and fouling test was initiated. Each fouling test ran for at least 16 hours with a filtrated volume of 450±50 mL. For

each set of experiments, three replicates were produced and the average values are reported

5.2.4 Analytical methods

Alginate concentration in feed solutions and permeate samples was measured using a Total Organic Carbon (TOC) analyzer (Shimadzu TOC-VCSH, Shimadzu Scientific Instruments, Japan). Calibration curves with R^2 values larger than 0.95 were constructed for the investigated systems (alginate; alginate and calcium; alginate and alum; alginate, calcium and alum), in order to correct any interference in the measurements. Volumetric size distribution of foulants was measured using laser diffraction (Mastersizer 2000, Malvern Instruments, Worcestershire, UK). Metal ions (calcium and aluminum) in the feed solution and permeate were measured using ICP-OES (Perkin Elmer Optima, Waltham, USA).

5.2.5 Resistances determination

Resistance in Series Model

In order to assess the fouling behavior of the investigated systems, resistances due to different fouling mechanisms were determined. Resistances were then calculated following the Resistance in Series Model, as shown in Equation 2.1.

Membrane hydraulic resistance, R_m , was determined by filtering DI water through virgin membrane sheets for at least 2 hours with the same operating conditions as mentioned in Section 5.2.3. Since the other resistances (R_a , R_p , R_c) did not exist at this stage, R_m was calculated using the following equation:

$$R_m = \frac{\Delta P}{\eta J_0} \quad (5.1)$$

where J_0 is the permeate flux of DI water filtered through the clean membrane. After this step, conditioning with background electrolyte (ionic strength of 10 mM as NaCl

and pH 7) was carried out for 2 hours. The same membrane sheet was then immersed with 50 mL of the feed solution and stirred at 100 rpm for 18 hours inside the filtration cell. This step allows the adsorption of foulant on the membrane surface. After the feed solution was removed, R_a was determined by filtering DI water through the ‘fouled’ membrane sheet for another 2 hours, and calculated by subtracting the hydraulic membrane resistance from the total resistance:

$$R_a = \frac{\Delta P}{\eta J'} - R_m \quad (5.2).$$

Here, J' denotes the permeate flux in the second step.

Resistances due to pore blocking and cake formation, R_p and R_c respectively, were determined concurrently; the same feed solution was filtered through the membrane sheet that had been previously used in the adsorption test for at least 16 hours, or until approximately 450 mL of the solution was filtered. The fouled membrane was then gently wiped with Kimwipes to remove the cake layer on the surface, and hence leaving only the foulants that blocked the pores. This method was described in detail by Tanaka et al. (1994). DI water was filtered once again through the same membrane sheets for 2 hours. Using the same algorithm as to calculate R_a , R_p was calculated as follows:

$$R_p = \frac{\Delta P}{\eta J} - R_m - R_a \quad (5.3),$$

where J denotes the permeate flux and the total resistance, R_t , equals to the first variable on the right hand side of the equation. Finally, R_c was calculated by subtracting all other resistances to the total resistance, R_t :

$$R_c = R_t - R_m - R_a - R_p \quad (5.4).$$

Specific Cake Resistance

Specific cake resistance was calculated using the MFI equation which was derived by Schippers and Verdouw (1980) as shown in Equation (2.4), with an assumption that there is no cake compression. A plot of t/V versus V was then constructed to determine I. As described by Schippers and Verdouw (1980), there exists three regions in the plot of t/V versus V , namely: (I) pore blocking region, (II) cake formation without compression, and (III) cake formation with compression (refer to Figure 2.3). The MFI parameter ($\eta I / 2\Delta P A^2$) was calculated by performing a linear regression in region (II) with R^2 larger than 0.95 and taking its slope as the value. Finally, specific cake resistance, α , was calculated by dividing the fouling index, I , with the bulk concentration of organic foulant in the feed solution, C_b (Lee *et al.* 2000; Schippers and Verdouw 1980) as shown in Equation (2.6).

5.2.6 Cake compressibility

Cake compressibility was assessed by measuring the cake compressibility factor, n , as described in (Lee *et al.* 2005d; Xu *et al.* 2004). These studies suggested that applied pressure may induce cake rearrangement, and with a greater scale of rearrangement (normally due to higher applied pressure), cake compression may occur. Cake compressibility factor was calculated using Equation (2.9). For this purpose, fouling experiments were conducted at 3 different pressures: 2.5 bar (250 kPa), 3 bar (300 kPa), and 3.5 bar (350 kPa), and the specific cake resistance was calculated using the MFI equation (Eq. 2.6). All other conditions were the same as stated in Section 5.2.3.

5.3 Results and Discussion

5.3.1 Flux decline trends, resistances and compressibility analyses

The permeate flux decline trends of the four investigated systems (sodium alginate; sodium alginate and calcium; sodium alginate and alum; sodium alginate, calcium and alum) are plotted in Figure 5.1. The most severe flux decline occurs in system

containing only sodium alginate, whereas the least severe occurs when alum is present in the system. The severity of flux decline decreases with the following order: (sodium alginate) > (sodium alginate, calcium) > (sodium alginate, alum) > (sodium alginate, calcium, alum). Contrary to some findings (Ang and Elimelech 2007; Jermann *et al.* 2007; Katsoufidou *et al.* 2007b), the addition of calcium improves the permeate flux relative to the base case, where only sodium alginate is present. This finding is in line with a study by (Ven *et al.* 2008), where it is suggested that calcium promotes the formation of highly permeable cake layer and the aggregation of alginate, both of which contribute to the lower cake resistance. These discrepancies will be discussed in details in Section 5.3.2.

Figure 5.1 Normalized flux declines of systems containing 30 mg/L sodium alginate, 1 mM calcium, 30 mg/L alum and their combinations. Feed solutions were prepared following the protocol in Section 2.1. Operating conditions: 25°C feed solution, TMP 350 kPa, pH 7 and ionic strength 10 mM as NaCl.

To further observe how each component affects various resistances, we conducted a resistance analysis. The results of this analysis are plotted in Figure 5.2, and the values are shown in Table 5.1. Our preliminary experiments show that the resistance

due to pore blocking, R_p , is close to 0. Hence, the resistances consist only of membrane hydraulic resistance, R_m , resistance due to adsorption, R_a , and resistance due to cake formation, R_c , all of which are plotted in percentage – relative to the total resistance. As shown in Figure 5.2, sodium alginate gives the largest R_c relative to the total resistance and higher R_a relative to the other systems, whereas the addition of calcium decreases both R_c and R_a . The addition of alum reduces R_c despite the presence of calcium, and the presence of calcium together with alum reduces R_a even more. This shows that the addition of calcium and/or alum could improve the permeate flux by reducing the resistances due to cake formation and adsorption.

Figure 5.2 Resistance analysis of the investigated systems: SA = sodium alginate, Ca = calcium, Al = alum. R_c , R_a and R_m denote the resistances due to cake formation, adsorption and membrane hydraulic resistance, respectively. Error bars indicate the range of data points (experiments were conducted in triplicates). Test conditions were the same as stated in Figure 5.1.

According to the particle size analyses, sodium alginate measures at around 0.3 (± 0.03) μm of average particle diameter. When 1 mM of calcium is added, aggregation of sodium alginate occurs, and the average particle diameter increases by one order of magnitude to 4.7 (± 3.5) μm . This shows that calcium indeed promotes the aggregation of sodium alginate.

Table 5.1 Resistance values summary of the investigated systems; α , R_c , R_m denote the specific cake resistance, cake resistance, and membrane hydraulic resistance respectively.

System ^a	$\alpha \times 10^{16}$ (m/kg)	$R_c \times 10^{13}$ (m ⁻¹)	$R_m \times 10^{13}$ (m ⁻¹)	R_c/R_m
SA	1.07 (± 0.003)	6.28 (± 1.0)	2.84 (± 0.2)	2.21
SA, Ca	0.69 (± 0.001)	4.06 (± 0.09)	2.81 (± 0.09)	1.44
SA, Al	0.23 (± 0.0006)	1.73 (± 0.09)	2.17 (± 0.04)	0.80
SA, Ca, Al	0.15 (± 0.0004)	1.34 (± 0.3)	2.78 (± 0.4)	0.48
Without Ca ^b	1.07 (± 0.003)	6.28 (± 1.0)	2.84 (± 0.2)	2.21
1 mM Ca	0.69 (± 0.001)	4.06 (± 0.09)	2.81 (± 0.09)	1.44
3 mM Ca	0.43 (± 0.001)	2.84 (± 0.06)	2.95 (± 0.06)	0.96
6 mM Ca	0.34 (± 0.0002)	1.75 (± 0.08)	2.96 (± 0.04)	0.59
Without Al ^c	1.07 (± 0.003)	6.28 (± 1.0)	2.84 (± 0.2)	2.21
10 mg/L Al	0.87 (± 0.002)	7.40 (± 0.4)	3.31 (± 0.09)	2.24
20 mg/L Al	0.49 (± 0.004)	6.23 (± 0.4)	3.04 (± 0.3)	2.05
30 mg/L Al	0.23 (± 0.0006)	1.73 (± 0.09)	2.17 (± 0.04)	0.80

^a The following concentrations and test conditions were applied: 30 mg/L alginate, 25°C, 350 kPa, 16 hours filtration time, pH 7, ionic strength 10 mM as NaCl, calcium and alum concentrations as indicated above. SA = sodium alginate, Ca = calcium, Al = alum.

^b In this set of experiments, alum was not present. 30 mg/L alginate was added and calcium concentration was varied as indicated above. Standard test conditions as in ^a were applied.

^c In this set of experiments, calcium was not present. 30 mg/L alginate was added and alum concentration was varied as indicated above. Standard test conditions as in ^a were applied.

As visually observed, the cake layer formed when calcium is present is more cohesively bounded as compared to when only sodium alginate is present; when the cake layer is gently sprayed with DI water, most of the cake layer of sodium alginate solution is washed away, whereas when calcium is present only a small amount of cake is washed away. This indicates that the positively charged calcium ions decrease the repulsive force between the negatively charged alginate molecules, hence making it easier to aggregate.

Another mechanism that promotes this aggregation is the preferential binding of calcium on the carboxylic functional groups of alginate, forming a structured network between adjacent alginate molecules that resembles an egg-box structure (Fang *et al.* 2007). Several researchers have proposed this Egg-Box model (deKerchove and Elimelech 2007; Fang *et al.* 2007; Grant *et al.* 1973). It is also suggested in those studies that this mechanism resulted in the gelation of alginate in the presence of calcium.

The addition of alum improves the permeate flux regardless the presence of calcium. Alum also decreases the cake resistance by 75% relative to the system containing only sodium alginate (Table 5.1) as a result of large flocs formed during coagulation/flocculation. Particle size measurements using laser diffraction show that these flocs are on the order of 500 μm of diameter in both sodium alginate-alum and sodium alginate-calcium-alum systems. Since particle diameter is inversely proportional to specific cake resistance as stated in the well-known Carman-Kozeny equation (as discussed in (Listiarini *et al.* 2009c)), the resulting permeate flux decline is less severe.

In order to investigate the dominant fouling mechanism in each system, a plot of ratio of filtration time and volume, t/V , as a function of filtered volume, V , is constructed (Figure 5.3). As seen in this figure, the first region of the curve (pore blocking, and possibly adsorption region) occurs at a short period of time at the beginning of each system, confirming our finding that R_a and R_p are negligible compared to R_c . The system containing only sodium alginate has a defined cake formation without compression region whose curve has the largest slope compared to the other 3 systems, indicating the largest specific cake resistance, α (Table 5.1). The addition of calcium decreases the specific cake resistance by approximately 30%, and the dominant fouling mechanism as shown in the MFI plot is cake formation without compression. When alum is introduced into the system, the specific cake resistance decreases even more. However, the plot of t/V versus V for this system does not show a defined second region. As suggested by (Katsoufidou *et al.* 2007b; Listiarini *et al.* 2009c), this result indicates that there might exist more than one dominant fouling mechanisms when alum is present, and that the cake is possibly compressible. The

system containing all three components (sodium alginate, calcium, alum) has the lowest specific cake resistance, implying that there is a synergistic effect between calcium and alum that results in more permeable cake layer.

Figure 5.3 MFI analysis of the investigated systems of sodium alginate, calcium, alum and their combinations; y-axis is the ratio of filtration time to the filtration volume, and x-axis is the filtered volume. Standard test conditions as in Figure 5.1 were applied. Dashed circle denotes the transition between Region I and Region II of the MFI equation.

Table 5.2 Compressibility analysis of the investigated systems: SA = sodium alginate, Ca = calcium, Al = alum. TMP was varied at 250, 300 and 350 kPa. Standard test conditions as stated in Figure 5.1 were applied, unless stated otherwise.

System	n	Remarks
SA	0.005	non-compressible
SA, Ca	0.002	non-compressible
SA, Al	0.323	slightly compressible
SA, Ca, Al	0.767	compressible

We looked further into the compressibility of the fouling layer in each system to justify the findings from the MFI plots as discussed above. To analyze the compressibility of the fouling layer, each run is conducted at three different pressures: 250, 300, and 350 kPa, and the equation for specific cake resistance as a function of TMP as described by Eq. (2.9) is obtained; when the n value is close to 0, the resulting fouling layer is incompressible, and when it is closer to 1 the layer is considered as compressible. As shown in Table 5.2, the n values of the first two systems (containing only sodium alginate and sodium alginate-calcium) are close to 0 ($n = 0.05$ and $n = 0.02$, respectively), and hence the fouling layers are incompressible, which confirms the dominant fouling mechanism obtained from the MFI plots (i.e. cake formation without compression). Although the addition of calcium results in larger particle size, the resulting incompressible cake suggests that the flocs formed are more compact/rigid compared to that formed in the presence of alum. In the system containing sodium alginate-alum, the n value is 0.323, which means that the fouling layer is slightly compressible. This is also in line with the MFI plots, since the cake formation without compression region is not clearly defined. One interesting note to point out is when alum is present together with calcium, the cake becomes compressible ($n = 0.767$). This implies that the synergistic effect of alum and calcium changes the characteristics of the cake layer into becoming more compressible and permeable.

5.2.1. Effect of calcium concentration on flux and resistances

As mentioned in Section 5.3.1, there are some discrepancies in the permeate flux decline trends of sodium alginate fouling when calcium is present; while some researchers found that the permeate flux decline is more severe with calcium (Ang and Elimelech 2007; deKerchove and Elimelech 2007; Katsoufidou *et al.* 2007b; Lee and Elimelech 2006), others (including this study) found the contrary (Ven *et al.* 2008). To further probe into the effects of calcium in sodium alginate fouling, a series of experiments were conducted with varied calcium concentrations of 1, 3, and 6 mM.

Figure 5.4 Effect of calcium concentration on normalized permeate flux. Feed solutions contained 30 mg/L alginate and varied calcium concentrations. Other test conditions: 25°C feed solution, TMP 350 kPa, pH 7 and ionic strength 10 mM as NaCl.

Figure 5.4 presents the permeate flux trends of systems containing sodium alginate and different calcium concentration. As seen in this figure, as calcium concentration increases, the permeate flux improves. In terms of resistance, an increase of calcium concentration from 1 to 6 mM decreases the relative cake resistance (R_c/R_m) by 60% and lowers the specific cake resistance by 50% (Table 5.1). The dominant fouling mechanism in this system as shown by the MFI plots (Figure 5.5) is cake formation without compression. As the calcium concentration increases, the fouling mechanism remains the same, and the slope of the curve decreases, which implies that the specific cake resistance also decreases.

Figure 5.5 Effect of calcium concentration on specific cake resistance. Y-axis is the ratio of filtration time to the filtration volume and x-axis is the filtration volume. Standard test conditions as in Figure 5.4 were applied. Dashed circle denotes the transition between Region I and Region II of the MFI equation.

These results could be explained by the larger particle size as calcium concentration is increased (i.e. two orders of magnitude increase in particle size, as calcium is increased from 0.5 to 1.5 mM), giving rise to lower resistance and hence permeate flux is higher. Another explanation for this is that calcium might be able to induce the formation of highly permeable polysaccharide gel layer (deKerchove and Elimelech 2007). In this study, it is found that at a certain ionic strength, the viscosity of solution containing sodium alginate decreases as the calcium concentration increases. Similar findings are also reported by (Ven *et al.* 2008), although the experiments were conducted at an elevated alginate concentration (500 mg/L alginate, as compared to 30 mg/L as in this study). Furthermore, competition between monovalent ions (sodium from background electrolyte) and divalent ions (calcium) may be the cause of the discrepancies of the permeate flux decline (deKerchove and Elimelech 2006, 2007). It is suggested that when divalent ions are more dominant than the monovalent ions, the resulting sodium alginate solution is more viscous. This results in larger resistances, and eventually could lead to severe flux decline. On the other hand, when monovalent ions are more dominant than the divalent ions, the solution becomes less

viscous hence resulting in improvement of permeate flux (deKerchove and Elimelech 2007). Another theory suggests that there might be an ion-exchange process occurring on the alginate gel layer, which replaces divalent ions with monovalent ions, eventually resulting in the breakup of the alginate gel network (Lee and Elimelech 2007).

In order to test this hypothesis, we performed a fouling test for 30 mg/L alginate and 1 mM calcium under a similar test conditions as stated in Figure 5.1 without adjusting the ionic strength to 10 mM as NaCl, such that calcium (divalent) ions become more dominant than sodium (monovalent) ions. It was found that the cake resistance (R_c) in the system where NaCl was not added is 30% larger than in the system with added NaCl. This suggested that the calcium ions were replaced by the sodium ions in the alginate gel layer, resulting in the swelling and break up of the alginate gel network (Lee and Elimelech 2007) and hence decreasing the cake resistance. This ion-exchange phenomenon has also been suggested by other studies (deKerchove and Elimelech 2007; Lee and Elimelech 2007; Ven *et al.* 2008).

5.3.2 Effect of alum concentration on flux and resistances

In order to look further into the fouling mechanism and resistances when alum is present in the system, we conducted a series of fouling experiments with different alum concentrations. In our previous study on humic acid fouling (Listiarini *et al.* 2009c), we have found that one or more fouling mechanisms occur at the same time when alum is present. In this study, we would like to observe whether this behavior is more pronounced when alum concentration is increased.

The normalized permeate flux trends as a function of filtered volume at different alum concentrations are shown in Figure 5.6. As alum concentration increases, the permeate flux decline is less severe. However, 10 mg/L of alum contributes to a similar value of normalized cake resistance (R_c/R_m) compared to the system containing only sodium alginate (Table 5.1), and the resistance values decrease as alum concentration increases. When alum is increased from 0 to 30 mg/L, the normalized cake resistance is reduced by 64% while the specific cake resistance is

reduced by 79%. This shows the effectiveness of alum in reducing the cake resistances by forming large and loose flocs during coagulation/flocculation (around 400 μm of average diameter particle) that forms a network of alginate-alum flocs. As mentioned earlier, the resulting cake layer in this system is compressible, yet permeable.

Figure 5.6 Effect of alum concentration on normalized permeate flux. Feed solutions contained 30 mg/L alginate and varied alum concentrations. Other test conditions: 25°C feed solution, TMP 350 kPa, pH 7 and ionic strength 10 mM as NaCl.

According to the MFI plots as shown in Figure 5.7, the dominant fouling mechanism in the system without alum is cake formation without compression, while when alum is added into the system, this fouling mechanism is not as apparent. This can be seen from the prolonged pore blocking region at the beginning of the filtration experiment. Although the cake formation without compression region can still be observed in alum concentrations of 10 and 20 mg/L, there does not seem to be a clearly defined second and third regions of the curve at alum concentration of 30 mg/L, which suggests that there might be more than one fouling mechanisms occurring at higher

alum concentrations. These findings also justify that alum is capable of changing the cake characteristics from non-compressible to more compressible.

Figure 5.7 Effect of alum concentration on specific cake resistance. Y-axis is the ratio of filtration time to the filtration volume and x-axis is the filtration volume. Standard test conditions as in Figure 5.6 were applied. Dashed circle denotes the transition between Region I and Region II of the MFI equation.

5.3.3 Schematic model

Based on our experimental results, the schematic model of sodium alginate, calcium, and alum fouling is proposed in Figure 5.8. Sodium alginate alone causes the largest flux decline and resistances. Although the dominant fouling mechanism is found to be cake formation, the cake layer of sodium alginate is not cohesively bounded due to the repulsive forces between foulant-foulant and foulant-membrane. When calcium is present in the system, aggregation of alginate is promoted and the resistances are smaller. Calcium also neutralizes the negatively charged alginate and membrane surface, giving rise to the cohesively bounded cake layer.

	System	Fouling characteristics	Fouling mechanism	Schematic model
1	Alginate	Large ΔJ Large R_c Large α Non-compressible	Cake formation
2	Alginate, calcium	Moderate ΔJ Moderate R_c Moderate α Non-compressible	Cake formation
3	Alginate, alum	Small ΔJ Small R_c Small α Slightly compressible	Undetermined (possibly pore blocking/ cake formation)
4	Alginate, alum, calcium	Small ΔJ Small R_c Small α Compressible	Undetermined (possibly pore blocking/ cake formation)

Figure 5.8 Schematic fouling model of (1) sodium alginate, (2) sodium alginate and calcium, (3) sodium alginate and alum, (4) sodium alginate, calcium and alum, on nanofiltration membranes.

The large and loose flocs formed in the presence of alum capture and bind the alginate together. Alum changes the characteristics of cake layer; the dominant fouling mechanism is no longer prominent and the cake becomes slightly compressible. When alum and calcium are present together, their synergistic effects result in more compressible cake layer, which has the lowest resistances compared to the other three systems. In terms of particle size, calcium does not significantly increase the alginate floc size. This indicates that calcium ions are bounded within the alginate molecules, all of which are captured inside the alum floc.

5.4 Conclusions

Fouling mechanism and resistances of systems containing sodium alginate, calcium, alum and their combinations have been schematically studied in this chapter. System containing only sodium alginate has the largest flux decline and resistances, while the addition of calcium and/or alum decrease both parameters. In contrary to some findings, it is found that calcium plays a role in improving permeate flux and decreasing resistances. It is further suggested that this is due to the dominance of monovalent ions (sodium) to divalent ions (calcium), which could result in the replacement of calcium ions by sodium ions in the alginate gel layer.

In systems where alum coagulant is added, it is observed that the fouling mechanism shifts from cake formation without compression to one or more mechanisms occurring at the same time (possibly pore blocking and cake formation with compression), as alum concentration increases. While alum results in slightly compressible cake layer and decreases the resistances, the presence of both alum and calcium has a synergistic effect and the resulting cake layer is more compressible with lower resistance values.

Chapter 6

High Molecular Weight NOM: Alginate – Part II

6.1 Introduction

As fresh water sources have become increasingly scarce, treating secondary wastewater effluent for indirect potable use has been considered and even applied in some countries. In advanced wastewater reclamation as well as drinking water treatment, NF technology has been widely used due to its capability in removing trace organic and inorganic contaminants (Escher et al., 2006; Pronk et al., 2006; Steinle-Darling and Reinhard, 2008; Wu et al., 2004a), while operating at lower pressure relative to RO

It is commonly known that fouling is inevitable in membrane filtration and is the major constraint of this technology, as it deteriorates the permeate quality and quantity and eventually results in shorter membrane life-spans. In advanced wastewater reclamation, organic matter in the form of biomass, NOM in drinking water sources, or synthetic organic matter produced by human activities may cause organic fouling and biofouling (Barker and Stuckey, 1999; Shon et al., 2006). Macromolecular and hydrophilic substances such as polysaccharide are considered as an important foulant in organic fouling of membrane filtration, and a number of studies have looked into polysaccharide fouling as modeled by sodium alginate (Jermann et al., 2007; Lee et al., 2006; Ven et al., 2008; Wang and Waite, 2008; Ye et al., 2005b).

Sodium alginate is a naturally derived polysaccharide from alginic acid extracted from brown algae and some species of bacteria, which comprises of linear copolymer of (1-4)-linked β -D-mannuronate (M) and α -L-guluronate (G) residues in alternating blocks (Fang *et al.* 2007). When calcium ions are present in the system, they will preferentially bind to the carboxylic functional groups of alginate and form gels with a structure resembling that of an egg-box (Grant *et al.* 1973). This highly compacted gel layer has been suggested to be the cause of severe permeate flux decline during membrane filtration of sodium alginate (Ang and Elimelech, 2007; deKerchove and Elimelech, 2007; Lee and Elimelech, 2006). However, some studies reported that calcium could help alleviate permeate flux decline, especially when fouling experiments were performed in dead-end filtration configuration (Listiarini *et al.* 2009b; Susanto *et al.* 2008; Ven *et al.* 2008). These discrepancies raised the question on how the different filtration conditions and configurations could result in different fouling trends, which is investigated in this study.

Coagulation as a pre-treatment to membrane filtration has been reported to improve permeate flux (Jung *et al.* 2006; Kimura *et al.* 2008; Lahoussine-Turcaud and Wiesner 1990), although others reported that the improvement of permeate flux is insignificant when nanofiltration membrane was used (Shon *et al.* 2005). However, none of these studied included calcium in their investigation. While calcium ions could be present naturally in water sources, calcium complexation with alginate may complicate the system even further. It is nevertheless important to investigate the fouling trends and permeate quality when alginate, calcium and alum coagulant are present in the system.

In an attempt to reduce the footprint of the water treatment plant, achieve higher NOM removal and maintain higher permeate flux, the use of hybrid coagulation-nanofiltration technique which combines coagulation process with nanofiltration has been reported (Listiarini *et al.* 2009b; Listiarini *et al.* 2009c). Since these studies were conducted in dead-end filtration configuration, the performance of this technique in terms of permeate flux decline, permeate quality and quantity when applied in cross-flow configuration as commonly practiced in water treatment and reclamation is investigated in this study. Resistance analysis was performed to assess the contribution of hybrid coagulation-nanofiltration to the total resistance. In addition,

fouling experiments were conducted at different calcium concentrations to understand the role of calcium in alleviating or severing the permeate flux during alginate filtration.

6.2 Materials and Methods

6.2.1 Chemicals

Sodium alginate from brown algae was purchased in powder form from Sigma-Aldrich (St. Louis, MO, USA) with a molecular weight ranging between 12-80 kDa as specified by the manufacturer. Stock solution of 3 g/L of sodium alginate was prepared for the fouling experiments, stored at 4 °C and discarded after 2 weeks. Pre-treatment of sodium alginate is as stated in Section 3.1.2.

Feed solution's pH was adjusted using 0.1 N HCl and 0.1 N NaOH. Ionic strength of the feed solution was adjusted to 10 mM using NaCl obtained from Fisher Scientific (Pittsburg, PA, USA). Reagent grade alum salts and calcium chloride used as the model coagulant and calcium ions, respectively. 0.02%-wt sodium azide (NaN_3) was added into the feed solution to prevent biofouling. Sodium hypochlorite (NaOCl) used in sodium alginate extraction was prepared from NaOCl solution containing 6-14% active chlorine.

6.2.2 NF membranes and bench-scale cross-flow nanofiltration setup

NF-270 membranes (Dow/FilmTec, Minneapolis, MN) were used throughout the fouling experiments. This polyamide thin-film composite membrane was stored in dry rolled sheets at 4 °C, and soaked in DI water for 48 hours prior to experiment. Properties of this membrane are listed in Section 3.1.1.

A bench-scale cross-flow nanofiltration setup consists of two 40 L feed tanks and two membrane testing cells configured in parallel (SEPA CF II, GE Osmonics,

Minnetonka, MN) as shown in Figure 3.4 was used throughout the study. Tank 1 was equipped with a mechanical stirrer (Cole-Palmer, Vernon Hills, IL). In this study, only Tank 1 was used as the feed tank throughout the experiment.

Each membrane cell houses a 14.5×9.7 cm membrane sheet. The channel height is 4 mm. After the membrane sheet, feed spacer and permeate carrier were loaded into the cell, the channel height was 2.8 mm. The cell holder must be pressurized prior to filtration experiment. In order to pressurize the cell holder, a hand pump (SPX Power Team, Rockford, IL) was connected to both cell holders to provide a pressure of 500 psi (3,450 kPa).

6.2.3 Fouling experiment and analyses

Fouling experiments

Filtration experiment was conducted for a total of 102 hours, including 30 hours of fouling test as shown in Table 3.3. Membrane hydraulic resistance, R_m , was calculated at the end of membrane compaction period. Conditioning with background electrolyte solution containing 10 mM NaCl was conducted afterwards. At 72 hour, foulant was added to the feed tank and fouling test was initiated. Fouling test lasted for 30 hours, and sampling was conducted at $t = 0, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 24$, and 30 hours. At the end of filtration experiment, fouled membrane sheets were carefully placed in a container and stored at 4 °C before performing sodium alginate extraction.

Analyses

Feed solutions were characterized for their viscosity and foulant size distribution. Viscosity was measured using a rotational viscometer (Rheolab MC1, Anton Paar, Ashland, VA) with a concentric cylinder for measuring low to medium viscous fluids. Each sample was measured either in triplicates or quadruplicates, with 50 mL volume of sample used in each measurement. The volumetric size distribution of foulants was measured using laser diffraction technique (Mastersizer 2000, Malvern Instruments, Worcestershire, UK).

Alginate accumulation on membrane surface was determined using extraction as described in Section 3.2.4. Alginate extraction was conducted using two methods: sodium hypochlorite method and calcium alginate method. Sodium hypochlorite method was used for extraction of sodium alginate, while calcium alginate method was used for systems where calcium was added.

Concentration of sodium alginate in the feed solution, permeate and extracted from the fouled membrane was measured using a total organic carbon analyzer (Shimadzu TOC-VCSH, Shimadzu Scientific Instruments, USA). Calibration standards with at least 8 points with triplicate standards for each point were prepared for each measurement. Calibration curves with R^2 values larger than 0.95 were constructed for each system, which includes alginate, alginate and calcium, alginate and alum, alginate, calcium and alum, to correct any interference in the measurements. Calibration standards of sodium alginate in 400 mg/L NaOCl solution were prepared for measurements of extracted alginate and to construct the calibration curve with R^2 values better than 0.95. For measurement of extraction samples by the calcium alginate method, calibration standards contained sodium alginate in NaOH solution were prepared.

ICP-OES with auto-sampler (Optima 2000 DV, PerkinElmer Optima, Waltham, MA) was used to measure aluminum, calcium and sodium concentrations in the feed and permeate solutions.

Resistance analysis was performed to assess the fouling behavior when calcium and/or alum were present together with sodium alginate, and to help understanding the interaction between sodium alginate and calcium. Resistances-in-series model was used to calculate the total resistance as shown in Eq. (2.1).

where the total resistance, R_t , equals the summation of all of the other resistances:

$$R_t = R_m + R_a + R_p + R_c \quad (6.1).$$

For simplicity, we define R_d as the resistance due to deposited materials on membrane surface, and is calculated by subtracting the total resistance with the membrane hydraulic resistance:

$$R_d = R_t - R_m \quad (6.2).$$

Membrane hydraulic resistance was calculated using Eq. (5.1). Specific cake resistance, α , was calculated using the ‘empirical’ formula, as shown in Eq. (2.5).

6.3 Results and Discussion

6.3.1 Hybrid coagulation-nanofiltration of sodium alginate in the presence of calcium

The permeate flux trends for the first 7 hours of filtration of feed solutions containing sodium alginate, calcium, alum and their combinations are shown in Figure 6.1. From this figure, it can be seen that the least severe permeate flux decline occurred during 30 mg/L sodium alginate filtration, while the most severe occurred when 1 mM calcium was present, with a total permeate flux decline after 30 hours of filtration of 68.9% and 88.6%, respectively, as shown in Table 6.2. The addition of alum (“hybrid coagulation-nanofiltration”) helped to improve the permeate flux relative to when alginate and calcium were present, with a permeate flux decline of 81.6% as compared to 88.6%. This suggests that hybrid coagulation-nanofiltration could be beneficial when calcium is present during filtration of sodium alginate. In the absence of calcium, the permeate flux decline of hybrid coagulation-nanofiltration after 30 hours was 75.5%, which is slightly lower than filtration of only sodium alginate (68.9%).

Figure 6.1 Normalized permeate flux trends for the investigated systems. Foulant concentrations and test conditions: 30 mg/L sodium alginate, 1 mM calcium, 30 mg/L alum, cross-flow velocity 15.3 cm/s, 24 ± 0.5 Bar, 25 ± 0.5 °C, pH 7 ± 0.5 , ionic strength 10 mM as NaCl. Values are averaged over four samples with error bars denoting one standard deviation, and shown if the value is larger than the symbol. Alg = sodium alginate, Ca = calcium, Al = alum.

These trends are different from the ones we observed during hybrid coagulation-nanofiltration of sodium alginate in dead-end configuration (Listiarini *et al.* 2009b). In general, cross-flow configuration is applied to reduce fouling and concentration polarization as compared to dead-end configuration. Since sodium alginate is not cohesively bounded with the membrane and the attachment is increased with the presence of calcium and/or alum (Listiarini *et al.* 2009b), cross-flow reduces the concentration polarization of sodium alginate and thus results in higher permeate flux when sodium alginate was filtered, relative to the systems where calcium and/or alum were present.

Table 6.1 Permeate flux decline and rejections for the investigated systems after 30 hours of fouling experiment.

System	Permeate flux	Rejection (%)			
	decline (%)	Alg	Na	Ca	Al
Alg	69.8	96.4 (± 2.1)	58.8 (± 1.5)	*	*
Alg+Ca	88.6	96.7 (± 2.5)	31.5 (± 9.6)	63.9 (± 3.1)	*
Alg+Al	75.5	99.1 (± 1.4)	37.9 (± 4.1)	*	99.7 (± 1.5)
Alg+Ca+Al	81.6	97.0 (± 2.7)	9.2 (± 8.6)	36.9 (± 23.2)	99.8 (± 0.5)

Note: Foulant concentrations and test conditions are as stated in Figure 6.1. Alg = sodium alginate, Na = sodium, Ca = calcium, Al = alum. * denotes that compound was not added into the feed solution.

As shown in Table 6.1, the rejection of sodium alginate by NF-270 membrane was 96.4%, due to the high molecular weight of alginate (12-80 kDa, as specified by the manufacturer) relative to NF-270 pore size (155 Da). This rejection did not change when calcium was introduced into the system, and was slightly higher when alum was added (higher than 97%). Through coagulation and flocculation, alum could form large flocs that capture sodium alginate and eventually were retained by the membrane, and hence alginate rejection is higher. In addition, alum was rejected more than 99% in all cases (Table 6.1).

Sodium rejection during alginate filtration is 58.8%, as shown in Table 6.1. This value, however, decreased to 31.5% when calcium was present in the system, and significantly decreased to 9.2% when both calcium and alum were present. Since NF-270 is negatively charged at pH around neutral (Tang and Leckie 2007), the addition of calcium and alum could modify the membrane surface charge into more positive (Listiarini *et al.* 2009c). Although the size of NaCl is smaller than the membrane pore size, rejection could be achieved through donnan (charge) exclusion (Seidel *et al.* 2001). When the membrane surface charge is close to neutral, sodium chloride molecules are less rejected by the membrane. This phenomenon could also be observed when adding calcium, where the rejection was 63.9% during alginate and calcium filtration, and decreased to 36.9% when alum was present in the system, where the membrane surface charge was possibly close to neutral. Another reason for

the decrease in sodium rejection is due to the increased solute concentrations at the membrane surface when calcium and/or alum are present. This will result in lower observed rejection as compared to the real or intrinsic rejection (Mulder 1996).

Figure 6.2 Ratio of resistance due to accumulation of foulant, R_d , to the membrane hydraulic resistance, R_m , of the investigated systems. Foulant concentrations and test conditions were as stated in Figure 6.1. Values are averaged over four samples with error bars denoting one standard deviation. Alg = sodium alginate, Ca = calcium, Al = alum.

Figure 6.2 shows the resistance analysis of the investigated systems. Normalization of resistance due to deposited materials on membrane, R_d , was performed since the hydraulic membrane resistance, R_m , for different membrane coupons may be slightly varied. As can be seen in the figure, filtration of only sodium alginate resulted in lowest normalized resistance compared to the other systems due to higher permeate flux, whereas the presence of both alginate and calcium resulted in highest normalized resistance. Addition of alum reduced the resistances by 48% when calcium was present, which suggests that alum could improve the permeate flux when filtering alginate together with calcium by forming large and loose flocs and hence reducing the resistances.

6.3.2 Effects of increasing calcium concentration

Figure 6.3 Normalized permeate flux trends for various concentrations of calcium. Foulant concentration and test conditions: 30 mg/L sodium alginate, cross-flow velocity 15.3 cm/s, 24 ± 0.5 Bar, 25 ± 0.5 °C, pH 7 ± 0.5 , IS 10 mM as NaCl (except for runs with 9 mM Ca where IS had exceeded 10 mM). Values are averaged over four samples with error bars denoting one standard deviation.

Effects on flux and resistances

The observed permeate flux and resistance of sodium alginate filtration in the presence of calcium seem to have a slightly different trend compared to the findings during filtration using dead-end configuration. In the previous study (Listiarini *et al.* 2009b), it was found that the addition of calcium would improve the permeate flux. However, in this study, it was observed that the addition of 1 mM calcium would result in severe permeate flux decline, although the permeate flux was improved as calcium concentration was increased, as can be seen in Figure 6.3. After 30 hours of filtration, the most severe flux decline occurred in filtration of 30 mg/L sodium alginate and 1 mM calcium (88% decline), whereas the least flux decline occurred in filtration of only alginate (69%), followed by alginate and 9 mM calcium (73%), as shown in Table 6.2. Although for both systems the increase of calcium concentration

will improve the permeate flux in general, it raises the question on how the different configurations may play a role in the discrepancies between permeate flux trends when calcium was present in alginate filtration.

Table 6.2 Permeate flux decline, accumulated mass and resistances for systems containing various concentrations of calcium after 30 hours of fouling experiment.

Calcium conc. (mM)	Permeate flux decline (%)	Accumulated mass (g/m ²)	$\alpha \times 10^{13}$ (m/g)
0	69.8	6.8 (± 1.4)	1.29 (± 0.28)
1	88.1	14.7 (± 1.6)	3.01 (± 1.18)
3	82.8	15.7 (± 3.8)	2.06 (± 0.38)
6	77.0	15.2 (± 1.2)	2.28 (± 0.73)
9	73.2	16.5 (± 1.3)	2.43 (± 0.36)

Note: Foulant concentration and test conditions are as stated in Figure 6.3. Values are averaged over at least four data with error bars denoting one standard deviation.

As seen in Table 6.2, the addition of calcium increases the attachment of alginate on membrane surface. Since both alginate and NF-270 membrane are negatively charged at around neutral pH, alginate is not cohesively bounded as can be seen from the low accumulated mass. Calcium ions could neutralize both alginate and the membrane surface and hence promoting the attachment of alginate. Based on the results, the increase of calcium concentration increases the accumulated mass on membrane. In terms resistances, the presence of calcium ions increases the specific cake resistance values; the highest increase was seen in filtration of alginate and 1 mM calcium, where the increase was more than 130%. This high specific cake resistance is also reflected in the permeate flux decline, where the decline for 1 mM calcium is the highest relative to the other systems. In general, the specific cake resistances are lower at calcium concentrations of 3 mM or higher, which translates to higher permeate flux. The possible causes of higher permeate flux during filtration of sodium alginate relative to when 1 mM calcium was present will be discussed in the following sections.

Table 6.3 Average floc size at various calcium concentration and IS.

Calcium conc. (mM)	Avg. floc size (μm) IS not adjusted	Avg. floc size (μm) IS=20 mM as NaCl
0	0.2	15.2
1	111.9	49.9
3	214.7	127.1
6	227.6	225.4
9	235.9	n.a.

Note: Experimental conditions: 30 mg/L sodium alginate, 15 rpm stirring speed, pH 7 and IS as stated. IS at Ca = 9 mM had already exceeded 20 mM.

Effects on floc size and solution viscosity

We then looked further into the changes in floc size and viscosity as calcium concentration increased. According to the Carman-Kozeny equation, the specific cake resistance, α , is inversely proportional to particle/floc diameter, d , to the power of two, which translates to higher permeate flux when floc size is larger, by having an assumption of incompressible cake layer (Carman 1938). As shown in Table 6.3, the average floc size increased with increasing calcium concentration. Calcium could neutralize the repulsive negatively-charged alginate chain and form bridges between adjacent molecules, and hence promotes the aggregation of alginate. This would result in improvement of permeate flux. The increase in floc size was obvious for low concentrations of calcium (0-3 mM), but not so for concentrations of 6 mM or higher. This might be due to exhaustion of carboxylic binding sites of alginate molecules at high concentration of calcium. When the solution's ionic strength was raised to 20 mM, as seen in Table 6.3, alginate floc size was smaller in general, except for the case where calcium was not present. In this case, ionic strength (in this case NaCl) could have a shielding effect on alginate molecules and make them less repulsive, resulting in aggregation of alginate molecules.

In terms of viscosity change, addition of calcium decreases the viscosity of sodium alginate quite significantly in the absence NaCl, as seen in Figure 6.4. As calcium concentration increases, the viscosity decreases even further. Some studies suggested that calcium might induce the gelation of alginate, which will lead to the formation of highly fluidic gel layer (Fang et al., 2007; Ven et al., 2008). In addition to this, we

have reported that the cake formed by alginate and calcium was incompressible (Listiarini *et al.* 2009b) which means that larger floc size would directly result in higher permeate flux. Therefore, a combination of larger floc size and lower viscosity in this case resulted in improvement of permeate flux in the presence of calcium. However, this does not seem to explain the higher permeate flux during filtration of only sodium alginate as compared to when 1 mM of calcium was present.

Figure 6.4 Normalized viscosities of systems containing various concentrations of calcium in 0.3 g/L sodium alginate solution at pH 7 and different ionic strengths. At calcium concentration of 9 mM, ionic strength value has exceeded 20 mM as NaCl. Values are averaged over at least three samples with error bars denoting one standard deviation.

One interesting point to note is that the solution viscosity was lower when measured at a higher ionic strength of 20 mM as NaCl, as shown in Figure 6.4. This might be due to ion exchange process between sodium and calcium ions, such that sodium ions replaced calcium ions, broke the alginate gel layer and resulted in swelling of the layer as suggested by (deKerchove and Elimelech, 2007; Lee and Elimelech, 2007). The most significant viscosity decrease occurred in sodium alginate solution, having a decrease of almost 30% when NaCl was present, which could be explained by the shielding effect caused by the salt and thus reduces the repulsion between alginate molecules as well as the coil dimension (Zhang *et al.* 1998). This suggests that ionic strength plays a major role in changing the alginate solution viscosity, especially in

the absence of calcium. It is likely that during sodium alginate filtration, concentration polarization (CP) of sodium chloride occurred along the membrane surface (i.e. boundary layer) causing the alginate viscosity to significantly decrease. Referring to Table 6.1, the rejection of sodium ions in the absence of calcium was 59% as compared to 32% when 1 mM calcium was present, and even lower (<10%) when calcium was 6 mM or higher (data not shown). This shows that the ionic strength at the boundary layer during filtration of sodium alginate alone might be higher compared to that of filtration of alginate and 1 mM calcium, resulting in significant decrease of sodium alginate viscosity. This could explain why the permeate flux was higher during filtration of only sodium alginate as compared to when 1 mM calcium was present. These results suggest that the permeate flux trends could be influenced by many factors such as foulant/ion rejection efficiencies and filtration unit configuration, in particular due to the counter-play between calcium, alginate and ionic strength (in this case NaCl). Furthermore, it is likely that the discrepancies between the observed permeate flux decline during sodium alginate filtration in the presence of calcium are due to the difference in what is occurring at the boundary layer.

Comparison between dead-end and cross-flow filtration configurations

In order to further justify the findings, the differences between dead-end and cross-flow filtration configurations were compared, and a suggestion of what might be happening at the boundary layer is given. As discussed in a study by (Fang *et al.* 2007), the change of solution viscosity is dependent upon the ratio of calcium to alginate concentration (or in particular, the G residue of alginate) in the solution, or $R = \text{Ca}/\text{G}$ (refer to Appendix C). For long chain alginates, the viscosity drops as R increases in the first step (until $R \sim 0.25$), increases in step II (until $R \sim 0.5$), and decreases again when R is larger than 0.55 (Figure 6.5). In particular, this phenomenon is interesting since it might explain the different calcium-alginate fouling behavior in both configurations.

Figure 6.5 Change of relative viscosity as a function of calcium to G residue ratio (R) for long chain alginates, as adopted from (Fang *et al.* 2007). DE = dead-end filtration configuration, CF = cross-flow filtration configuration.

During dead-end filtration, concentration polarization of alginate is much higher compared to cross-flow, as alginate is >96% rejected and cross-flow velocity does not exist. These result in high concentration of alginate at the boundary layer, which translates to low R (step I region). On the other hand, concentration polarization in cross-flow configuration is not as severe such that alginate accumulation at the boundary layer is smaller, and hence R is higher. It is likely that the cross-flow configuration in this study falls into step III, resulting in high viscosity at lower concentration of calcium and subsequently decreases as the concentration of calcium increases. When the R values were calculated by incorporating the rejection of alginate and calcium, and estimating the G-residue of sodium alginate from Sigma-Aldrich by using available data (Chhatbar *et al.* 2009; Russo *et al.* 2007), the smallest R value in the experiments was well above 0.55 for calcium concentration of 1 mM and was subsequently larger for higher concentrations (please refer to Appendix C), which confirms that the system falls into step III region of Figure 6.5. Other studies that observed the decrease of permeate flux with increase of calcium concentration might have a boundary layer condition that falls into step II region, where the relative viscosity increases with the increase of R .

6.3.3 Schematic model of calcium interaction with alginate

Based on the permeate flux decline trends in both dead-end and cross-flow configurations, floc size and viscosity measurements, the interaction between sodium alginate molecules and calcium ions at different ionic strengths and calcium to G residue ratios (R) is proposed, as shown in Figure 6.6. These two parameters (ionic strength and R) are seen to have a major role in determining the permeate flux trend during filtration of sodium alginate and calcium, more importantly the parameters at the boundary layer where concentration polarization occurs.

At low ionic strength and low R value, sodium alginate molecules are repulsive to each other (as shown in '1' of Figure 6.6). At this condition, the chains have an open conformation and the solution viscosity is high. When calcium is present at low concentration ('2'), calcium ions will form bridges between adjacent alginate molecules, forming an organized egg-box structured, and the resulting solution viscosity is high. These two conditions ('1' and '2') lead to severe permeate flux decline, which was observed during filtration of sodium alginate in dead-end configuration, and sodium alginate and 1 mM calcium using cross-flow configuration, respectively. At low R value and high ionic strength, as seen in '3', ion exchange process between sodium and calcium ions occurs. This causes the alginate chains to break open and swell, resulting in low solution viscosity and smaller floc size.

When the calcium concentration is high and the ionic strength is low, there exists more aggregation between alginate molecules ('4'). This leads to formation of larger flocs which result in less severe permeate flux decline during filtration. Low solution viscosity and high permeate flux at this condition suggests that the gel layer formed during filtration may be more fluidic and permeable. At high R value and high ionic strength ('5'), ion exchange process breaks the egg-box structure of alginate, leading to swelling of the structure. This also causes alginate to aggregate less, as suggested by the smaller floc size. These resulted in low solution viscosity which could lead to improvement of permeate flux.

Figure 6.6 Schematic illustration of calcium interaction with alginate at different ionic strengths and R-values.

6.4 Conclusions

In this study, hybrid coagulation-nanofiltration for removal of sodium alginate in the presence of calcium has been investigated, and the interaction between calcium and alginate has been systematically studied. In particular, some conclusions that can be drawn from this study are as follows:

1. Hybrid coagulation-nanofiltration during sodium alginate removal could be beneficial when calcium ions are present in the systems since alum could reduce the resistances and improves the permeate flux. The improvement of flux, however, is more prominent in dead-end configuration as compared to cross-flow.

2. Interaction between calcium and alginate is influenced by factors such as ionic strength and concentrations. The increase of calcium concentration in alginate solution will lower the viscosity and increase the aggregation between alginate molecules. The increase in ionic strength will lower the viscosity and decrease the aggregation between alginate molecules, as the ion exchange process between sodium and calcium ions will result in swelling and breaking up of the gel layer.
3. The discrepancies between the observed fouling trends during alginate and calcium filtration are possibly due to the different conditions (i.e. ionic strength, concentration ratio of calcium to alginate) at the boundary layer. It is most likely that different filtration configurations (dead-end vs. cross-flow) could create different conditions for this interaction.

Chapter 7

Hybrid Coagulation-Nanofiltration for Removal of Bromide and Bromate

7.1 Introduction

Bromide is naturally occurring in raw water with the highest reported concentration found in drinking water source at 2 mg/L (Cowman and Singer 1996). Although this compound is not regulated, it is commonly associated with the production of bromate which is currently classified by the United States Environmental Protection Agency (USEPA) as potentially carcinogenic inorganic substance, with a maximum contaminant level (MCL) of 0.010 mg/L (Pontius 2003). This substance is an oxidation product of bromide by ozone, OH radicals or a combination of both, during ozonation of waters containing background bromide concentration (Pinkernell and von Gunten 2001). A study by Von Gunten and Salhi (2003) shows that bromate production is proportional to the concentration of bromide in raw water and ozone dosage, while other factors such as amount of NOMs, pH and alkalinity of water determine the threshold concentration of bromate (Siddiqui *et al.* 1995). In addition, although bromate is not naturally present in surface waters, the presence of bromate in rivers, possibly as a result of industrial activities, has been reported (Butler *et al.* 2005).

In the drinking water treatment train, bromate could be produced during pre-ozonation of raw water containing bromide (Figure 7.1). Pre-ozonation is conducted as a pre-treatment to the membrane filtration process in order to minimize the organic matter loading (Lee *et al.* 2005c). Another possible point of bromate production in the drinking water treatment train is during disinfection, at the last step of treatment (Figure 7.1). Bromate formation could be minimized by adding ammonium (NH_3) to react with hypobromous acid (HOBr), an intermediate product of bromide oxidation to bromate, to produce monobromamine (NH_2Br) and interfere the oxidation pathway (Pinkernell and von Gunten 2001). Alternatively, the solution pH can be lowered such that the equilibrium of HOBr/OBr^- is shifted towards HOBr (Von Gunten and Salhi 2003). Other bromate removal methods such as coagulation, reduction, UV and activated carbon have been reported (Ge *et al.* 2007; Kimbrough and Suffet 2002; Sanchez-Polo *et al.* 2006; Zhang *et al.* 2009), including nanofiltration (NF) (Chellam 2000; Chellam *et al.* 2008; Prados-Ramirez *et al.* 1995). However, these methods are impractical or not effective for large-scale application. Hence, there is an urgent need to look for an alternative cost effective solution to resolve the problem of bromate in water.

Figure 7.1. Drinking water treatment diagram. Dashed circles show the points where bromate could be formed.

Membrane filtration has been widely applied in drinking water treatment. Combination of NF with other treatment techniques such as coagulation to provide high quality water is ongoing (Listiarini *et al.* 2009b; Listiarini *et al.* 2009c; Steinle-Darling *et al.* 2007). Organic matter is commonly removed via coagulation process using coagulating agents such as aluminum sulphate, and the flocs formed are removed via filtration. It has been shown that coagulation as a mean of pre-treatment of membrane processes offers advantages such as reduction of coagulant dose, mixing-time, energy consumption and head loss, and has been found to effectively remove organic matter while maintaining high flux recovery (Lee *et al.* 2000; Shon *et al.* 2005).

It has been reported earlier that combining NF and coagulation (“hybrid coagulation-nanofiltration”) is advantageous in effectively rejecting natural organic matter and divalent cations, as well as significantly reducing the cake resistance (Listiarini *et al.* 2009c). However, there is still lack of knowledge in the capability of this technique in removing bromide or bromate together with NOM. Although bromate is the target compound to be removed due to its suspected carcinogenic properties, the possibility and feasibility of removing bromide prior to formation of bromate are also crucial to be studied, in order to design the suitable cost effective removal strategies. Therefore, this study aims at investigating the possibility of bromide, bromate and NOM removals by hybrid coagulation-nanofiltration technique. This study is divided into three parts: (1) removal by nanofiltration membrane, (2) removal by coagulation, and (3) removal by hybrid coagulation-nanofiltration, in order to observe the techniques individually as well as their synergistic effects. In particular, this study explores the added values of hybrid coagulation-nanofiltration, and will provide insights on the novel techniques of removal of contaminants in the drinking water treatment train.

7.2 Experimental Section

7.2.1 Chemicals and membranes

Commercial HA was purified prior to use according to modified IHSS purification method as described in Section 3.1.2. Stock solution of 0.3 g/L was prepared from PAHA by diluting with DI water. This solution was filtered with 1 μm fiberglass filters to remove the impurities. The filter was changed with a new one after 5 minutes of filtration to minimize the loss of humic acid on the filter. The resulting stock solution was stored in the dark at 4 °C and discarded after 3 months. Bromide and bromate stock solutions were prepared from reagent grade sodium bromide (NaBr) and sodium bromate (NaBrO₃) salts, respectively. Stock solutions of 10 mM sodium bromide and 4 mM sodium bromate were prepared and kept at 4 °C.

Reagent grade alum salts (Al₂(SO₄)₃·14-18H₂O) and ferrous sulphate (FeSO₄) were used as the coagulating agents. Stock solution of 10 g/L alum was prepared prior to the experiments and stored at 4 °C, while ferrous sulphate was added in solid form. Bromide and bromate standard solutions were purchased from Fischer Scientific (Pittsburg, USA). Solution pH and ionic strength were adjusted using sodium hydroxide, hydrochloric acid, and sodium with concentrations of 0.1 N, 0.1 N and 10 mM, respectively.

Two types of NF membranes (NF-270 and NF-90, supplied by Dow FilmTec) were used in this study. As summarized in Table 3.1, NF-270 is looser compared to NF-90 with a smooth membrane surface, and consequently its pure water flux is higher (Tang and Leckie 2007). NaCl rejection in NF-90 is higher compared to NF-270 due to its smaller pore size, which makes it a good option for rejecting ions such as bromate. As shown by the contact angle and zeta potential values, NF-270 is more hydrophilic and more negatively charged, and therefore less susceptible to fouling.

7.2.2 Filtration unit and rejection experiments

The filtration and rejection experiments were conducted in a dead-end filtration unit as shown in Figure 3.3. Membrane sheet was firstly soaked in DI water for at least 2 days. To begin the experiment, DI water was passed through the membrane until the flux remained stable, which usually took about 2 hours and serves as a baseline for the subsequent filtration experiments. After that, a 2-hour sodium chloride conditioning was applied to reach the equilibration with background electrolyte at the desired pH and ionic strength. Each run is conducted for at least 16 hours or until all the solutions in the feed tank was filtered (150 ± 25 mL). Each set of experiment was conducted in triplicates to ensure the reproducibility of the results.

7.2.3 Jar test and analytical methods

Jar tests were conducted using a flocculator with 6 stirrers in order to investigate the removal of bromide/bromate as well as humic acid by coagulation. Each jar containing 300 mL of solution was prepared as stated elsewhere (Listiarini *et al.* 2009c). After overnight settling, the solution's supernatant was carefully drawn using a syringe and analyzed for humic acid and bromide/bromate concentrations.

Humic acid content was measured using a UV/Vis spectrophotometer (Shimadzu UV-1700, Kyoto) at a wavelength of 254 nm. Bromate and bromide concentrations in the feed and permeate solutions were measured using an ion chromatography (IC) with 38 mM NaOH eluent (Dionex ICS-1000, Dionex Corporation, Sunnyvale, CA) and an IonPac AS15 analytical (4 x 250 mm) column (Dionex ICS-1000, Dionex Corporation, Sunnyvale, CA). ICP-OES with auto-sampler (Optima 2000 DV, PerkinElmer Optima, Waltham, MA) was used to measure the aluminum and iron concentrations in the feed and permeate solutions. Each sample was measured in five replicates, and the reported values were the averages of the five replicates.

7.2.4 Flux and resistance calculations

Permeate flux and resistances analyses were conducted to evaluate the performance of each combination of hybrid coagulation-nanofiltration. The Resistance in Series Model was applied to estimate the total resistance during filtration experiment as shown in Equation (2.1).

Membrane hydraulic resistance, R_m , was obtained during the first step of filtration experiment by filtering DI water through a clean membrane coupon for 2 hours at 3.5 Bar (350 kPa) and calculated using Equation (5.1).

The resistance due to the deposited materials on the membrane surface, R_d , was calculated by subtracting the total resistance to the membrane hydraulic resistance, as shown in Equation (6.2).

7.3 Results and Discussion

7.3.1 Removal by nanofiltration

In the first part of the experiments, removals of bromide, bromate and humic acid were conducted by means of nanofiltration alone in order to see the effectiveness of this method. Normalized permeate fluxes (J/J_0) of NF-270 and NF-90 were found to be 0.3 (-) and 0.8 (-), respectively, at the end of 15 mg/L HA filtration at 350 kPa. Due to the low permeate flux of NF-90 membranes, each filtration experiment using this membrane was conducted for at least 16 hours, or until 150 ± 25 mL of the feed solution was filtered. In contrary, filtration experiment using NF-270 with the same filtered volume took around 9 hours to complete.

In this study, bromide, bromate and humic acid were filtered individually and combined to see whether there was any interaction that could lead to higher or lower removal efficiencies. Previous study has shown that bromate could be removed up to 77% using nanofiltration alone (Prados-Ramirez *et al.* 1995).

Table 7.1 Removal of HA, bromide and bromate using nanofiltration at the following concentrations and test conditions: 15 mg/L HA, 0.05 mM Br⁻, 0.02 mM BrO₃⁻, pH 7, ionic strength 10 mM as NaCl, TMP 350 kPa.

System	HA removal (%)	Br removal (%)	BrO ₃ removal (%)
<i>NF270</i>			
Br	**	1.3 (±0.59)	**
BrO ₃	**	**	5.9 (±0.98)
HA	70.7 (±0.01)	**	**
HA+Br	77.9 (±2.07)	2.41 (±0.26)	**
HA+BrO ₃	77.9 (±0.68)	**	5.23 (±2.37)
<i>NF90</i>			
Br	**	6.9 (±0.67)	**
BrO ₃	**	**	18.9 (±1.86)
HA	94.0 (±4.59)	**	**
HA+Br	87.6 (±7.65)	6.4 (±2.57)	**
HA+BrO ₃	91.8 (±6.18)	**	18.6 (±1.72)

** indicates that the compound was not added into the system.

We have found in this study, however, that nanofiltration could not effectively remove bromide or bromate, as shown in Table 7.1. Both NF-270 and NF-90 membranes could only remove 1% and 7% of bromide, respectively and 6% and 19% of bromate, respectively. In contrary, humic acid was effectively removed by nanofiltration (Table 7.1); NF-270 and NF-90 had removed up to 71% and 94% of humic acid, respectively. These results are expected since the MWCO of the membranes are much higher than the hydrated radii of bromide and bromate (0.231 and 0.229 nm, respectively), as shown in Figure D.1 of Appendix D; NF-270 and NF-90 have MWCOs of 155 and 100 Da, respectively, which translates to around 16 and 10 nm of pore diameters. When bromide or bromate was filtered together with humic acid, the removal efficiencies for bromide, bromate as well as for humic acid did not change significantly. This suggests that there was no interaction between bromide, bromate and humic acid that could result in significant change of removal efficiency.

7.3.2 Removal by coagulation

Table 7.2 Removal of HA, bromide and bromate using coagulation. Alum and FeSO_4 concentrations were 30 and 150 mg/L, respectively. HA, Br and BrO_3 concentrations were 15 mg/L, 0.05 mM and 0.02 M, respectively.

System	HA removal (%)	Br removal (%)	BrO_3 removal (%)
<i>Alum</i>			
HA	96.9	**	**
HA+Br	97.7	Not removed	**
HA+ BrO_3	95.8	**	24.1
HA+Br+ BrO_3	98.1	Not removed	22.4
<i>FeSO_4</i>			
HA	76.6	**	**
HA+Br	97.7	Not removed	**
HA+ BrO_3	97.2	Not removed	100.0 (<i>n.d.</i>) [#]
HA+Br+ BrO_3	97.1	Not removed	100.0 (<i>n.d.</i>)

[#]*n.d.* denoted that the compound was not detected in the supernatant.

Removal of bromide, bromate and humic acid by coagulation was performed using two different coagulants: aluminum sulphate (alum) and ferrous sulphate. Prior to the experiments, jar tests were conducted to find the concentrations of both coagulants that give similar humic acid removals at the presence of bromide or bromate. This step is necessary since we are comparing two different types of coagulant. Firstly, the concentration of alum coagulant was fixed at 30 mg/L, which gave around 97% of humic removal when bromide or bromate was present. Next, three concentrations of ferrous sulphate (50, 100, 150 mg/L) were tested and it was found that the concentration of 150 mg/L was the one that gave around 97% of humic removal when bromide or bromate was present.

In the next step, the removals of bromide, bromate and humic acid were observed in four different systems: only humic acid (HA), humic acid and bromide (HA+Br), humic acid and bromate (HA+ BrO_3), and humic acid, bromide and bromate (HA+Br+ BrO_3) for each of the coagulant. As can be seen in Table 7.2, although alum coagulant could effectively remove humic acid (more than 96%), it could not remove

bromide at all and could only remove around 20% of bromate. The slightly better removal of bromate by alum coagulation might be due to the larger molecular weight of bromate (MW: 127.9 g/mol) as compared to bromide (MW: 79.9 g/mol), as shown in Table D.1, which makes it easier for bromate to be caught by the precipitation net of alum and subsequently settled down with the flocs. A study by Ge *et al.* (2007) reported a higher value of bromide removal by alum coagulant (around 20%) at pH 7, 15 mg/L alum, 2.0 mg/L bromide and 6 mg/L humic acid.

Similar to alum, ferrous sulphate could also not remove bromide from the solution, as shown in Table 7.2. The removal of humic acid was relatively good, with the lowest removal of 77% when only humic acid was present. However, when bromate was added into the solution and coagulation/flocculation/settling was performed, bromate was no longer detected in the supernatant. In the systems where 0.02 mM bromate was added (HA+BrO₃ and HA+Br+BrO₃), the supernatant only contained bromide (total bromide concentrations of 0.006 mM and 0.054 mM, respectively, with initial bromide concentration of 0.05 mM for the latter) and there was no bromate detected in the solution. This suggests that bromate was reduced by ferrous ions into bromide, following the reaction (Siddiqui *et al.* 1994):

while the rest of the unreduced bromate might be removed by coagulation and retained by the membrane.

As can be seen from the reactions, ferrous ions were oxidized into ferric ions which eventually precipitates in the form of Fe(OH)₃, and this compound functions as a coagulating agent (Butler *et al.* 2005). After around 30 minutes of flocculation, flocs of Fe(OH)₃ were formed and could be observed in the solution. This reduction-oxidation process was also observed in the solution containing humic acid, bromide and bromate, where no bromate ions were detected in the supernatant after coagulation process (Table 7.2). These results suggest that reduction-oxidation

process of bromate by ferrous sulphate is effective in reducing bromate, while ferric coagulant as a result of the redox reaction could effectively remove humic acid.

7.3.3 Removal by hybrid coagulation-nanofiltration

Table 7.3 Normalized flux decline of the investigated systems. Test conditions are the same as stated in Table 7.1. HA, Br, BrO₃, alum and FeSO₄ concentrations were 15 mg/L, 0.05 mM, 0.02 M, 30 mg/L and 150 mg/L, respectively.

System	Flux decline (%)	
	NF-270	NF-90
HA	48.6	65.9
HA + Al	18.1	58.2
HA + Fe	55.5	69.9
HA + Br	46.5	75.9
HA + Br + Al	36.9	79.6
HA + Br + Fe	54.4	61.5
HA + BrO ₃	42.3	72.1
HA + BrO ₃ + Al	26.6	73.8
HA + BrO ₃ + Fe	48.7	64.6

As shown in Table 7.3, the use of alum coagulant in NF-270 membranes could improve the permeate flux relative to the non-hybrid systems. This improvement, however, is not observed when NF-90 membrane was used, unless during filtration of only humic acid, where the flux decline was reduced from 65.9% to 58.2%. On the other hand, the use of ferrous sulphate coagulant resulted in more severe flux decline when combined with NF-270 membrane as compared to the non-hybrid systems. Interestingly, the permeate flux is less severe or even improved when ferrous sulphate is combined with NF-90 membrane. In the case of humic acid and bromate filtration, the permeate flux decline was reduced from 72.1% to 64.6% by hybrid coagulation-nanofiltration using ferrous sulphate and NF-90. In addition to improving permeate flux, applying this technique will also reduce bromate ions to bromide, and at the same time removing more than 98% of humic acid (Table 7.4).

Table 7.4 Removal of humic acid, bromide and bromate by hybrid coagulation-nanofiltration. Test conditions and concentrations are as stated in Table 7.3.

System	HA removal (%)		Br removal (%)		BrO ₃ removal (%)	
	NF-270	NF-90	NF-270	NF-90	NF-270	NF-90
<i>Alum</i>						
HA	98.9 (±0.13)	98.7 (±0.38)	**	**	**	**
HA+Br	98.6 (±0.26)	99.1 (±0.16)	1.3 (±0.67)	17.8 (±5.6)	**	**
HA+BrO ₃	98.3 (±0.52)	99.4 (±0.32)	**	**	9.1 (±2.1)	11.1 (±1.9)
<i>FeSO₄</i>						
HA	99.7 (±0.10)	99.1 (±0.04)	**	**	**	**
HA+Br	98.9 (±0.33)	98.7 (±0.31)	4.9 (±1.6)	16.4 (±11.8)	**	**
HA+BrO ₃	99.2 (±0.20)	98.2 (±0.37)	**	**	100 (<i>n.d.</i>) [#]	100 (<i>n.d.</i>)

[#]*n.d.* denoted that the compound was not detected in the supernatant.

The permeate quality in terms of removal of humic acid, bromide and bromate by hybrid coagulation-nanofiltration is shown in Table 7.4. This technique was able to remove more than 98% of humic acid in all cases (NF-270 or NF-90, combined with either alum or FeSO₄), which was an improvement compared to when either coagulation or nanofiltration was used individually. As seen in Table 7.4, hybrid coagulation-nanofiltration with alum could only achieve 10% of bromate removal, which shows that alum coagulation combined with nanofiltration is not effective in removing bromate. In comparison, bromate was reduced to bromide when FeSO₄ was added, while the unreduced portion was possibly retained by the coagulated flocs and membrane, since there was no bromate detected in permeate. On the other hand, bromide was found at around 0.005 mM and 0.003 mM for hybrid coagulation-nanofiltration using NF-270 and NF-90, respectively. This means that bromide could not be effectively removed by this technique, having the highest removal at only 17% when NF-90 was used. This suggests that the removal of bromide prior to formation of bromate is not feasible compared to removing bromate after it is being formed. When the reduction of bromate to bromide by hybrid coagulation-nanofiltration is applied in drinking water treatment train, caution must be taken in choosing the disinfection method post-membrane filtration such that brominated DBPs will not re-occur. On top of effectively removing bromate, humic acid and maintaining the permeate flux, hybrid coagulation-nanofiltration is able to reduce the footprint of the

treatment plant, and could be implemented by a simple modification of the treatment process.

7.3.4 Resistance analysis

Finally, resistance calculation was conducted to calculate how much resistance was increased or decreased when applying hybrid coagulation-nanofiltration for removal of humic acid, bromide and bromate. Normalized values of R_d to R_m were used to assess the increase or decrease of R_d relative to R_m , and are necessary to compare between membranes that have different R_m values.

Table 7.5 Comparison of resistance values between hybrid and non-hybrid systems using NF-270 membranes.

System	$R_m \times 10^{13} \text{ (m}^{-1}\text{)}$	$R_d \times 10^{13} \text{ (m}^{-1}\text{)}$	$R_d/R_m \text{ (-)}$	Change of $R_d/R_m \text{ (%)}$ *
HA	2.03 (± 0.058)	2.43 (± 0.064)	1.19	*
HA + Al	2.42 (± 0.208)	1.12 (± 0.290)	0.46	-61.3
HA + Fe	2.81 (± 0.223)	4.43 (± 1.049)	1.58	32.8
HA + Br	2.21 (± 0.079)	2.20 (± 0.616)	0.99	*
HA + Br + Al	2.32 (± 0.162)	1.73 (± 0.475)	0.75	-24.2
HA + Br + Fe	2.89 (± 0.231)	6.09 (± 2.837)	2.11	113.1
HA + BrO ₃	2.21 (± 0.069)	2.33 (± 0.608)	1.05	*
HA + BrO ₃ + Al	2.44 (± 0.227)	1.31 (± 0.305)	0.54	-48.6
HA + BrO ₃ + Fe	2.74 (± 0.166)	4.05 (± 0.895)	1.48	40.9

* Change of R_d/R_m was calculated based on the system where coagulant was not added.

For example, in the system containing HA, BrO₃, Fe/Al, the change of R_d/R_m was calculated relative to HA and BrO₃.

Table 7.5 shows the effect of hybrid coagulation-nanofiltration on the resistances when using NF-270 membranes. It was previously reported that the hybrid coagulation-nanofiltration using alum could decrease the specific cake resistance by 40% during filtration of 30 mg/L of humic acid (Listiarini *et al.* 2009c). In this study, however, while the addition of alum coagulant could reduce R_d/R_m value up to 61% when filtering only humic acid, it was not the case with ferrous sulphate coagulant.

Hybrid coagulation-nanofiltration using ferrous sulphate could increase R_d/R_m value to more than 100% of the non-hybrid system containing humic acid and bromide. Despite the high increase of R_d , the normalized permeate flux in this system was not affected significantly, as shown in Table 7.3. In the system containing humic acid and bromate, hybrid coagulation-nanofiltration using FeSO_4 increases R_d/R_m by 41%, with an advantage of reducing bromate into bromide.

When NF-90 membranes were used in hybrid coagulation-nanofiltration, we would expect to see much higher values of R_d relative to that in NF-270 membranes, as can be seen in Table 7.6. It is interesting to note that hybrid coagulation-nanofiltration using alum coagulant with NF-90 membranes would result in higher R_d/R_m ratio compared to that in non-hybrid systems, except for the system containing only humic acid where there was a 13% decrease. The highest increase of R_d/R_m ratio in hybrid coagulation-nanofiltration with alum coagulant was observed in filtration of humic acid and bromate. However, this did not significantly affect the flux decline (Table 7.3) with a flux decrease of 72% in the non-hybrid system as compared to 74% in the hybrid system.

Referring to Tables 7.5 and 7.6, hybrid coagulation-nanofiltration using ferrous sulphate coagulant and NF-90 membranes did not increase R_d/R_m ratio as much as that with NF-270 membranes, which can be seen as an advantage; the highest increase of R_d/R_m ratio was 22% as opposed to 40.9% when using NF-270. Although these results are preliminary, they are nevertheless important since they give insights to the possibilities of applying hybrid coagulation-nanofiltration in removal of bromate and NOM, and at the same time maintaining and even improving the permeate flux. Since membrane filtration and coagulation are widely applied in drinking water treatment, the application of hybrid coagulation-nanofiltration is feasible by choosing the suitable membrane and coagulant.

Table 7.6 Comparison of resistance values between hybrid and non-hybrid systems using NF-90 membranes.

System	$R_m \times 10^{13} \text{ (m}^{-1}\text{)}$	$R_d \times 10^{13} \text{ (m}^{-1}\text{)}$	$R_d/R_m \text{ (-)}$	Change of $R_d/R_m \text{ (%)}$
HA	5.34 (± 0.411)	16.8 (± 4.26)	3.15	*
HA + Al	6.13 (± 0.721)	16.8 (± 5.04)	2.74	-13.0
HA + Fe	5.18 (± 0.339)	15.3 (± 4.34)	2.95	-6.3
HA + Br	4.95 (± 0.409)	14.7 (± 4.23)	2.97	*
HA + Br + Al	5.23 (± 0.650)	15.7 (± 5.19)	3.00	1.0
HA + Br + Fe	5.30 (± 0.680)	17.4 (± 4.63)	3.28	10.4
HA + BrO ₃	5.00 (± 0.350)	14.1 (± 3.53)	2.82	*
HA + BrO ₃ + Al	5.12 (± 0.059)	18.2 (± 0.050)	3.55	25.9
HA + BrO ₃ + Fe	5.11 (± 0.059)	17.6 (± 4.882)	3.44	22.0

7.4 Conclusions

This study has systematically investigated the hybrid coagulation-nanofiltration technique in removing humic acid, bromide and bromate. It was found that coagulation or nanofiltration alone could not effectively remove humic acid, bromide and bromate. Hybrid coagulation-nanofiltration is seen as a potential technique to be applied in drinking water treatment system for its capability in effectively removing humic acid and reducing bromate to bromide when ferrous sulphate is used, and at the same time maintaining and even improving the permeate flux. While bromide removal is not effective with either one of the techniques, bromate could be completely reduced to bromide by ferrous sulphate, while ferrous itself was oxidized to ferric and acted as coagulant. This indicates that the removal of bromide prior to formation of bromate is not feasible compared to removing bromate after it is being formed. When the reduction of bromate to bromide by hybrid coagulation-nanofiltration is applied in drinking water treatment train, caution must be taken in choosing the disinfection method post-membrane filtration such that brominated DBPs will not re-occur.

Results from this study confirm that the efficiency of hybrid coagulation-filtration technique is influenced by factors such as types of membrane and coagulant. Future work based on these results is needed to evaluate other factors that could influence the effectiveness of this technique, and to find the combination of membrane and coagulant that could improve the permeate flux even more while having high removals of humic acid and bromate.

Chapter 8

Conclusions, Contributions and Future Work

8.1 Conclusions and Contributions

This chapter consists of general conclusions of Chapters 4 to 7, as the more specific conclusions are already presented in the corresponding chapters. The topic of this research was initiated with a thought of looking at the interaction between NOM, calcium and alum in order to investigate the possibilities of applying hybrid coagulation-nanofiltration in removing NOM when calcium was present. As coagulation is a common pre-treatment for membrane filtration and has been shown to improve permeate flux, I would like to find out whether combining coagulation and filtration processes (or the so-called ‘hybrid coagulation-nanofiltration’ technique) would be both beneficial and feasible to be applied in drinking water treatment process.

The first part of this research was to observe humic acid fouling during dead-end nanofiltration, which has been intensively studied. During the investigation of fouling trends and foulant-membrane attachment using humic acid as model NOM as discussed in Chapter 4, it was found that the use of alum coagulation improved the permeate flux significantly despite the presence of calcium due to the decrease of resistances. These findings suggest that coagulation-nanofiltration is potential to be applied for removal of NOM and calcium, particularly using a dead-end filtration configuration. In addition, a correlation between foulant-membrane attachment to the ratio of empirical and theoretical specific cake resistance was developed.

Based on the findings, a new attachment coefficient for the MFI equation was proposed. This part of study was considered as the initial step in understanding foulant-foulant and foulant-membrane interactions, particularly in an environment where NOM, calcium and alum are present simultaneously, which represents the real condition in the drinking water treatment process.

The next step of the research was to expand the investigation into looking at other type of NOM, which is commonly found in secondary wastewater effluent and contributes greatly to organic and biofouling – extracellular polymeric substances (EPS). EPS is commonly modeled by sodium alginate, a type of polysaccharide that behaves similarly to EPS during filtration. Sodium alginate is particularly interesting to study since it forms a specific structure called the ‘egg-box’ structure when interacting with calcium ions. Since this gel structure is believed to be compact and dense, analog to bridging between humic acid molecules by calcium ions that results in a compact fouling layer, many researchers suggested that the structure was responsible for the severe permeate flux decline during filtration of sodium alginate and calcium. Interestingly, others found that the presence of calcium could actually improve permeate flux. Based on these discrepancies, I have looked at fouling of sodium alginate and calcium in two different filtration configurations – dead-end and cross-flow – and in particular studied the interaction between sodium alginate and calcium. I have also conducted an investigation to observe whether hybrid coagulation-nanofiltration would behave similarly in both configurations.

As discussed in Chapters 5 and 6, the results showed that the hybrid coagulation-nanofiltration of sodium alginate behaved similarly to filtration of humic acid in dead-end configuration, where the addition of alum could greatly improve the permeate flux. This behavior, however, was not observed during hybrid coagulation-nanofiltration of sodium alginate using cross-flow configuration. These findings suggest that the different configurations could result in different performance of hybrid coagulation-nanofiltration during filtration of the same feed solution in terms of severity of fouling and permeate flux trends. In addition to this, the different behavior between the two configurations was even more apparent during filtration of sodium alginate and calcium; although in general permeate flux was improved with the increase of calcium concentration, it was observed that sodium alginate filtration

resulted in better permeate flux in cross-flow compared to that in dead-end configuration. This result, however, is reversed when low concentration of calcium was present. I then looked further into how the different configurations could create different conditions, possibly at the boundary layer of the membrane, which leads to the different flux decline trends. With regard to this, it was suggested that the conditions (i.e. ionic strength, solute concentrations) at the boundary layer play a major role in determining fouling and permeate flux decline trends. In this study, I have proposed the interaction between sodium alginate and calcium at different ionic strengths and ratios of solute concentrations, in order to describe what happened at the boundary layer. It was concluded that the discrepancies of permeate flux trends during filtration of sodium alginate and calcium are due to the different conditions created at the boundary layer.

The last part of the research is exploring the added value of hybrid coagulation-nanofiltration in removing disinfection by products (DBPs) alongside NOM as discussed in Chapter 7. Bromate was particularly chosen as the DBP to be removed due to its suspected human carcinogenic properties and the fact that it is commonly found in drinking water treatment train after ozonation of waters containing bromide. In this study, I also explored the possibilities of removing bromide prior to bromate formation in order to design the most suitable removal strategies, and for this purpose, different membrane and coagulant types were tested. It was found that different membrane and coagulant types could influence the performance of hybrid coagulation-nanofiltration and that the removal of bromide prior to formation of bromate is not feasible compared to removing bromate after it is being formed. With this technique, reduction of bromate to bromide and improvement of permeate flux were achieved, as well as effective removal of NOM. In addition, the use of hybrid coagulation-nanofiltration is advantageous since it could be further expanded for DBPs removals through simple modification of treatment processes and selection of proper coagulant. However, caution must be taken in choosing the disinfection method post-membrane filtration such that brominated DBPs will not re-occur.

8.2 Future Work

As the demand for fresh water is constantly rising and fresh water sources have become increasingly scarce, indirect potable use of treated secondary wastewater effluent has been considered and even applied in some countries. NF technology is seen as a promising technology in drinking water treatment and advanced wastewater reclamation due to its capabilities in removing trace organic and inorganic contaminants, while operating at lower pressure compared to reverse osmosis. While space is always limited in many large cities where municipal water and wastewater treatments are located, the trend of treatment technology is going towards the direction where treatment is more effective and footprint is smaller. This is where hybrid technologies come into play.

Although combining coagulation and membrane filtration is not novel in drinking water and wastewater treatment technologies, there is lack of information on the interaction between NOM with calcium when coagulation process is occurring, and its relation to the extent of nanofiltration membrane fouling. Based on the work presented in this thesis, several studies should be conducted in the future in order to achieve improvements of hybrid coagulation-nanofiltration and develop fouling mitigation techniques:

While dead-end filtration configuration is convenient to use and the unit scale makes some parameters relatively easier to control, there exists a paramount difference between cross-flow and dead-end filtration configurations: different conditions created at the boundary layer. Up to date, there is no study focusing on the concentration profile at the boundary layer and along the membrane surface, in particular during filtration of NOM, calcium and coagulant. There is also lack of knowledge on the interparticle forces between NOM and calcium in the presence of coagulant. Furthermore, there is no systematic study on how these forces relate to the fouling extent of nanofiltration membranes. By understanding these further, the fouling mechanisms, solutes rejections, and the interaction between NOM-calcium-coagulant could be deduced.

In terms of hybrid coagulation-nanofiltration technique, there are many possibilities for further studies. One could optimize this technique by choosing the proper membrane and coagulant in order to serve different purposes, or investigate other factors that could influence the performance of hybrid coagulation-nanofiltration. In addition to this, one could also explore other added values of hybrid coagulation-nanofiltration, for example in removals of other emerging contaminants alongside NOM while maintaining higher permeate flux. A systematic investigation on the impact of floc size, charge of deposit, thickness of deposit and the impact of speciation at different pH on removals of DBPs or other emerging contaminants should also be conducted in order to enlighten the removal mechanisms of hybrid coagulation-nanofiltration.

Conceptual models of fouling in complex systems containing NOM, coagulant and calcium could be supported by surface analyses using techniques such as Transmission Electron Microscopy (TEM). It is important to note, however, that pre-treatment of sample in this technique plays a critical role since it might affect the intactness of the sample.

In cross-flow nanofiltration, simulation could be performed in order to distinguish between concentration polarization and Donnan exclusion with regard to ion rejection mechanisms. It might be also interesting to look at how the Ca to G residue ratio relates to viscosity. This could be investigated by looking at various sodium alginates with different M/G values. In addition, a hydrodynamic study that compares the condition at the boundary layer (for e.g. concentration, thickness, etc.) in cross-flow and dead-end configurations could help decipher the different observed flux trends in these two systems.

Other possible study that might not be directly related to this research is on the development of novel membrane materials that could mitigate fouling and achieve high efficiencies of solutes rejection. However, one must take into account the feasibility of the new membrane materials to be applied in the water treatment system and whether complicated modification of the treatment process is required.

Although there are still many works to be done in this field and even more questions to answer, this study contributes nevertheless to the knowledge of complex nature of coagulation process and unique interaction of calcium and NOM for the purpose of fouling mitigation. As Professor Anthony Fane once said, “fouling goes hand-in-hand with successful filtration”, there is always room for improvement.

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Appendix A

Calibration Curves

Figure A.1 Typical calibration curve for determination of sodium chloride concentration using the conductivity of solution.

Figure A.2 Typical TOC calibration curve for alginate concentration determination. Calibration was performed prior to each measurement.

Figure A.3 Calibration curve for UV adsorption at 254 nm for pretreated humic acid (PAHA) concentration determination, for concentrations ranging between 1 to 15 mg/L.

Appendix B

Supplementary Data Associated with Chapter 5

Figure B.1 Plot of t/V versus V of 30 mg/L sodium alginate fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Figure B.2 Compressibility coefficient calculation of 30 mg/L sodium alginate fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Figure B.3 Plot of t/V versus V of 30 mg/L sodium alginate and 1 mM calcium fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Figure B.4 Compressibility coefficient calculation of 30 mg/L sodium alginate and 1 mM calcium fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Figure B.5 Plot of t/V versus V of 30 mg/L sodium alginate and 30 mg/L alum fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Figure B.6 Compressibility coefficient calculation of 30 mg/L sodium alginate and 30 mg/L alum fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Figure B.7 Plot of t/V versus V of 30 mg/L sodium alginate, 1 mM calcium and 30 mg/L alum fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Figure B.8 Compressibility coefficient calculation of 30 mg/L sodium alginate, 1 mM calcium and 30 mg/L alum fouling at different trans-membrane pressures (2.5, 3 and 3.5 Bar). Other operating conditions are as stated in Figure 5.1.

Table B.1. Reproducibility results example of particle size measurements. Samples contained 30 mg/L sodium alginate, 1 mM CaCl₂ and 50 mg/L alum. Only cycles 50-99 were included (refer to Section 3.2.5). d(0.5) denotes the particle size diameter corresponding to the 50th percentile. d(0.5)-1 measurement was conducted on Feb. 25, 2008 and d(0.5)-2 was conducted on Feb 26, 2008 (continued to p. 140).

Cycle	d(0.5)-1 (μm)	d(0.5)-2 (μm)
50	953.9	988.0
51	1003.1	856.2
52	905.3	825.2
53	1053.4	782.0
54	966.2	1144.2
55	981.8	971.8
56	849.6	1057.8
57	1131.2	894.4
58	920.9	1242.9
59	1010.4	904.0
60	820.9	1080.8
61	938.9	986.1
62	1005.6	908.4
63	1025.2	1064.2
64	993.5	1111.1
65	839.6	1168.9
66	963.1	888.0
67	966.2	1252.0
68	945.5	782.5
69	1067.0	1085.7
70	1194.8	816.5
71	900.6	969.0
72	938.3	764.0
73	1082.4	1038.7
74	1017.5	917.0
75	891.4	811.5
76	1044.2	961.8
77	1010.2	884.8
78	1031.7	836.0
79	828.1	853.0
80	1020.3	950.3
81	987.1	995.9
82	1009.8	722.8
83	784.5	755.9
84	863.2	955.9
85	1224.4	1023.8
86	902.3	897.0
87	1068.6	926.8
88	883.1	918.0
89	754.7	1025.5
90	862.1	797.3
91	1058.7	860.1
92	915.0	713.6
93	599.4	794.3
94	1029.4	855.8
95	907.4	815.0
96	1029.1	978.1
97	960.3	652.6

APPENDIX B. SUPPLEMENTARY DATA

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98	959.8	891.3	
99	824.9	611.0	
	958.5	919.7	Average (μm)
	109.7	139.9	Std deviation (μm)

Appendix C

Calcium to G Residue Ratio ($R=Ca/G$) Calculation

Sodium alginate comprises of linear copolymer of (1-4)-linked β -D-mannuronate (M) and α -L-guluronate (G) residues in alternating blocks. Mannuronate to Guluronate ratio (M/G) of sodium alginate could be determined, for example, using conventional hydrolysis method with strong acidic solutions or newer methods such as microwave irradiation (Chhatbar *et al.* 2009).

In this study, however, the M/G ratio was determined based on the available references for Sigma-Aldrich sodium alginate, in which G residue values are between 55-68% of sodium alginate mass ((Chhatbar *et al.* 2009; Russo *et al.* 2007).

By incorporating the rejection of sodium alginate and calcium (96.7% and 63.9%, respectively, refer to Table 6.2) and by taking the smallest G residue values for lower limit estimation, for 30 mg/L sodium alginate and 1 mM of $CaCl_2$ in solution we get:

$$Ca/G = (0.639 \times 40 \text{ mg/L}) / (0.967 \times 0.55 \times 30 \text{ mg/L}) = 1.6$$

which is well above the third region limit of 0.55 in Figure 6.5. Please note that the effect of concentration polarization that occurs at the boundary layer will cancel out,

C. CALCIUM TO G RESIDUE RATIO CALCULATION

since concentration polarization will occur for both sodium alginate and calcium. In summary, for calcium concentrations ranging between 1-9 mM we get:

Table C.1 Ratio of calcium to G residue of sodium alginate at different calcium concentrations. Ca = calcium, Alg = alginate. Alginate concentration is 30 mg/L.

Ca conc. (mM)	Ca rejection (%)	Alg rejection (%)	R = Ca/G
1	63.9	96.7	1.60
3	15.4	99.2	1.13
6	33.3	94.7	5.11
9	33.1	94.9	7.61

This calculation shows that the cross-flow configuration falls within the third region of Figure 6.5 since all of the R values are larger than 0.55.

Appendix D

Characteristics of Bromide and Bromate

Table D.1. Molecular weight, ionic radius and hydrated radius of bromide (Br^-) and bromate (BrO_3^-) (Marcus 1991).

Characteristics	Br^-	BrO_3^-
MW (g/mol)	79.9	127.9
Ionic radius (nm)	0.196	0.191
Hydrated radius (nm)	0.231	0.229

Appendix E

Cake Characterization of Sodium Alginate Fouling of Nanofiltration Membranes in the Presence of Calcium and Alum

*Submitted to Water Science and Technology: Water Supply

E.1 Introduction

In recent years, nanofiltration (NF) technology has been gaining considerable attention especially in the application of drinking water and wastewater treatments. NF membranes are considered as a promising technology in drinking water and wastewater treatments due to its lower operating pressure as compared to reverse osmosis (RO) and smaller pore size as compared to ultrafiltration (UF). One of the major drawbacks in membrane filtration is organic fouling by natural organic matter (NOM) which causes a decline in both permeate quality and quantity. In secondary wastewater effluent, organic fouling is mainly caused by the effluent organic matter (EfOM), which constitutes of a wide range of compounds, among which are polysaccharides that form a significant component of extracellular polymeric substances (EPS) (Barker and Stuckey 1999; Duncan *et al.* 2000; Manka *et al.* 1974).

In addition, the presence of calcium as ionic constituents of natural and wastewaters may complicate the system even further since calcium preferentially binds to the carboxylic functional groups of alginate molecules and thus results in gel formation of alginate (Katsoufidou *et al.* 2007b).

In the drinking water and wastewater treatment trains, NOM is commonly removed via coagulation/flocculation processes with the aid of a coagulating agent such as aluminum sulphate (alum). The addition of alum is found to alleviate the flux decline despite more cake layer is formed along the membrane surface, which gives insights to the possibilities of hybrid coagulation-nanofiltration application as a decentralized system in water treatment technology (Lee *et al.* 2000; Li and Elimelech 2004; Shon *et al.* 2005). Although some studies have looked into filtration systems containing coagulants and divalent cations, there is lack of knowledge of the fouling mechanism and cake characteristics in these systems.

This study systematically investigates the fouling mechanism and cake characteristics of sodium alginate, calcium, alum, and their combinations in a dead-end nanofiltration system. Blocking Filtration Law, MFI and the Carman-Kozeny equations are used to evaluate the fouling mechanisms and to estimate the cake porosity, resistances and thickness. Results in this study would provide more insights in direct filtration of secondary wastewater effluents using nanofiltration technology.

E.2 Materials and Methods

E.2.1 Chemicals and membranes

All chemicals used were of analytical grade, unless stated otherwise. A commercial sodium alginate (Sigma-Aldrich, St. Louis, MO) extracted from brown algae was used throughout the experiments. A stock solution containing 3 g/L of sodium alginate was prepared by dissolving the sodium alginate in DI water, followed by filtration through 0.45 μm Nylon membrane to eliminate the amount of large flocs or impurities that could influence the accuracy of the experiments. Calcium chloride,

CaCl_2 , and aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, were also obtained from Sigma-Aldrich and used as calcium and alum components, respectively. Sodium chloride, NaCl (Sigma-Aldrich, St. Louis, MO) was used as a background electrolyte. pH of the feed solution was adjusted using hydrochloric acid, HCl , and sodium hydroxide, NaOH , both obtained from Sigma-Aldrich.

A commercial thin-film composite NF membrane, denoted as NF-270 by the manufacturer (Dow-Film Tec, Minneapolis, MN), was used in the fouling experiments. NF-270 is negatively charged at around neutral pH (Tang *et al.* 2007c), has a molecular weight cut-off of 155 Da and NaCl rejection of 40% (as specified by the manufacturer), and is relatively hydrophilic with a contact angle value of 32° (Manttari and Pekuri 2002). Membrane samples were soaked in DI water and stored at 4°C for at least 48 hours prior to fouling experiments.

E.2.2 Filtration unit and fouling experiments

Fouling experiments were carried out using a dead-end filtration unit as shown in Figure 3.3. The dead-end nanofiltration unit consisted of an 800 mL reservoir tank, 50 mL stainless steel stirred tank, and a weighing scale connected to a data logger. Pressure was provided by compressed nitrogen gas. A constant trans-membrane pressure was applied at 3.5 Bar (350 kPa) throughout the experiment, and pH and ionic strength of the feed solution were adjusted to 7 and 10 mM as NaCl respectively. Sodium alginate, calcium and alum were added at concentrations of 30 mg/L, 1 mM and 30 mg/L respectively. Each run was conducted for at least 16 hours or until all the solutions in the feed tank was filtered (450 ± 50 mL).

Fouling experiments were performed for the four investigated systems: (1) sodium alginate; (2) sodium alginate and calcium; (3) sodium alginate and alum; (4) sodium alginate, calcium, and alum. The membrane was firstly stabilized and equilibrated with DI water for at least 2 days. To begin the experiment, DI water was passed through the membrane until the flux remained stable, which usually took about 2 hours and served as a baseline for the subsequent fouling experiments. After that, a 2-hour sodium chloride conditioning was applied to reach the equilibration with background

electrolyte at the desired pH and ionic strength. Next, after feed solution was prepared, fouling experiment was carried out for 16 hours. To ensure the reproducibility of the experiments, runs were conducted in triplicates for each system.

E.2.3 Analytical methods

Feed solutions and permeate samples were measured for their alginate concentration using Total Organic Carbon (TOC) analyzer (Shimadzu TOC-VCSH, Shimadzu Scientific Instruments, USA). Floc and particle size were measured using laser diffraction technique (Mastersizer 2000, Malvern Instruments, Worcestershire, UK).

Specific cake resistance, α , was calculated using the MFI equation (Schippers and Verdouw 1980). MFI equations were derived based on the cake filtration theory, which is the cake filtration portion of the blocking filtration law. For this purpose, a plot of ratio of filtration time to the filtration volume (t/V) versus the filtration volume (V) was constructed. MFI was calculated from the linear portion of this plot, following the equation given in Schippers *et. al.* (1980):

$$\frac{t}{V} = \frac{\alpha C_b}{2\Delta P A^2} V + \frac{\eta R_m}{\Delta P A} \quad \text{Eq. (C.1),}$$

where V is the filtrate volume, t is the filtration time, ΔP is the applied trans-membrane pressure, μ is the permeate viscosity, R_m is the membrane hydraulic resistance, A is the effective membrane surface area, α is the specific cake resistance and C_b is the bulk concentration of foulant in the feed solution.

Blocking Filtration Law derived by (Hermia 1982) as shown in Table E.1 was used to characterize the fouling mechanisms. Plots were constructed for each mechanism and linear regression was performed to see which fouling mechanism was dominating by looking at the largest value of R^2 (square of correlation coefficient).

Table E.1 Fouling mechanisms and their corresponding characteristics and equations, derived in Blocking Filtration Law (Hermia 1982).

Filtration laws	Characteristics	Equations
Cake filtration	All particles are accumulated in a cake layer.	$\frac{t}{V} = aV + b$
Intermediate blocking	Particles are allowed to settle on previously deposited particles.	$-\ln\left(\frac{J}{J_o}\right) = at + b$
Standard blocking	All particles settled inside the pores.	$\frac{1}{J} = at + b$
Complete blocking	Each filtrated particle participates in blocking the membrane.	$\frac{t}{V} = at + b$

After the specific cake resistance, α , was obtained using the MFI equation, cake porosity and cake thickness were estimated using equations derived from the Carman-Kozeny equations (Eqs. E.2-3) (Faibish *et al.* 1998), where K'' is the empirical Kozeny constant (typically $K''=5$), ρ_p is the particle density, d_p is the mean diameter of particle, ε is the cake porosity, δ is the cake thickness, and R_c is the resistance due to cake formation:

$$\alpha = \frac{36K''(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \quad \text{Eq. (E.2)}$$

$$\delta = \frac{R_c}{\alpha \rho_p (1-\varepsilon)} \quad \text{Eq. (E.3)}$$

E.3 Results and Discussion

E.3.1 Fouling mechanism

As shown in Figures E.1a-d, all four curves of the different fouling mechanisms were plotted on one graph along with their corresponding linear regressions. As seen in Figure E.1a, the fouling mechanism of sodium alginate could not be characterized by a single fouling mechanism across the whole range of flux decline since the correlation values are more than 0.95, except for complete blocking mechanism. While pore blocking mechanisms are significant in this system, it was found that cake filtration played a dominant role in the fouling process, indicated by the highest R^2 values, which ranged from 0.993 to 0.995 (Table E.2). This suggests that at the initial stage of filtration, pore blocking mechanism was responsible for fouling. This was then followed by cake filtration mechanism that dominated over the filtration period.

The same procedure was carried out to assess the fouling mechanism of system containing alginate and calcium (Figure E.1b). It can be seen that the highest R^2 value occurred for cake filtration, followed by the standard pore blocking (Table E.2, Figure E.1b). Similar to alginate fouling, at the beginning of filtration all of the membrane pores were blocked by alginate-calcium molecules, and as the filtration time progressed the cake layer built up and hence cake filtration mechanism dominated.

Figure E.1 Fouling mechanism analysis using the Blocking Filtration Law of the investigated systems: (a) sodium alginate; (b) sodium alginate and calcium; (c) sodium alginate and alum; (d) sodium alginate, calcium and alum. Concentrations used were 30 mg/L alginate, 1 mM calcium and 30 mg/L alum. Other experimental conditions: TMP 3.5 Bar, ionic strength 10 mM as NaCl and pH 7.

For systems containing alum, the dominant fouling mechanism could not be depicted from the blocking filtration law; all four mechanisms have R^2 values of less than 0.8. Although none of the four fouling mechanisms fitted well over the entire fouling process of sodium alginate and alum, pore blocking followed by cake filtration is suggested as the dominant fouling mechanisms in this system. A study by Ye et al. (2005) also suggested that in this particular system there existed a two-stage fouling

processes of pore blocking and cake filtration. When calcium was present together with alum, the dominant fouling mechanism was standard pore blocking followed by cake filtration, although it is not clearly shown by the R^2 values. These fouling mechanisms were observed more clearly in the filtration of alginate and calcium, where the R^2 values for standard pore blocking and cake filtration are larger than 0.93. These results suggest that alum is capable of changing the characteristics of fouling mechanism from cake filtration/pore blocking to the co-existence of all fouling mechanisms.

Table E.2 Square of correlation coefficient (R^2) of different fouling mechanisms based on the Blocking Filtration Law of the four investigated systems. Concentrations used were 30 mg/L alginate, 1 mM calcium and 30 mg/L alum. Experimental conditions were as stated in Figure E.1.

System/Run		R^2				
		Cake filtration	Complete pore blocking	Intermediate pore blocking	Standard pore blocking	Dominant mechanism
Alginate	1	0.995	0.721	0.963	0.963	Cake filtration
	2	0.969	0.822	0.965	0.931	
	3	0.993	0.853	0.964	0.963	
Alginate, Calcium	1	0.977	0.817	0.87	0.945	Cake filtration
	2	0.969	0.822	0.965	0.931	
	3	0.978	0.899	0.466	0.932	
Alginate, Alum	1	0.746	0.616	0.762	0.718	Undetermined
	2	0.712	0.545	0.6	0.689	
	3	0.716	0.557	0.612	0.692	
Alginate, Calcium, Alum	1	0.577	0.437	0.462	0.565	Undetermined
	2	0.699	0.61	0.672	0.677	
	3	0.581	0.442	0.465	0.569	

E.3.2 Cake Characterization

In this study, cake layer formed in the four investigated systems was characterized for its specific cake resistance, porosity, and resistance due to cake formation in order to assess the fouling behavior of the investigated systems. As shown in Table E.3, the presence of alum decreased the specific cake resistance, α , and resistance due to cake formation, R_c , compared to the system containing only sodium alginate. This might be due to the increase of particle diameter, which has a strong correlation to the specific cake resistance. According to the Carman-Kozeny equation and as shown in Equation E.2, specific cake resistance is inversely proportional to particle diameter to the power of two, or $\alpha \sim d_p^{-2}$. The difference between the theoretical and experimental specific cake resistance may be attributed to the ideality of conditions assumed in the equation (for e.g. laminar flow, perfectly spherical rigid spheres, etc.).

The addition of calcium also decreased the resistances, although not as much as when alum was present. The increase of particle diameter in the system containing alginate and calcium, which suggests that there was aggregation of alginate due to the presence of calcium, might contribute to the decrease of the resistances. It is suggested that alginate forms a gel network when calcium is present resulting in egg-box like gel structure (Katsoufidou *et al.* 2007b). In addition to this, we have found earlier that at a certain ionic strength, the presence of calcium may decrease the viscosity of the solution, leading to higher permeate flux and consequently lower cake resistance (Listiarini *et al.* 2009a). This finding is in line with another study by Ven *et al.* (2008) The presence of both alum and calcium decreased the resistances even further to less than 10% compared to that when only sodium alginate was present.

While Carman-Kozeny equation (Eqs. E.2 and E.3) is based on assumptions of rigid particles and laminar flows which might not be the case in real systems, it could give an estimation of the cake porosity and thickness in these systems. In this study, we used $K'' = 5$ in the calculation since K'' is close to this value for many different beds

(Richardson *et al.* 2002). Although $K'' = 5$ holds for typical porosities of 0.3-0.5, we have done iterations to ensure that K'' and ε values converge. According to our estimation, the cake porosity decreased when alum and/or calcium were added into alginate solution, as shown in Table E.3. In contrast, we have found in our previous work that the addition of calcium and/or alum improved the permeate flux (Listiarini *et al.* 2009a), which suggests that porosity might not be the main parameter that governs the permeability of the gel layer. It is suggested by (Wang and Waite 2008) that the network structure of the gel layer plays a more dominant role in controlling the permeability than the cake porosity. In addition, when alum was present in the system, cake porosity decreased by more than two orders of magnitude. A study by Lee *et al.* (2003) suggested that the cakes formed by large particles/flocs (of more than 40 μm) are permeable, regardless of whether the flocs formed are compact or loose. This means that the large flocs formed in our systems were possibly loose and susceptible to compression, which is shown by the low cake porosity. This is in line with our findings that alum is capable of changing the cake characteristics into more compressible (Listiarini *et al.* 2009a).

Table E.3 Cake characteristics (specific cake resistance, α ; porosity, ε ; resistance due to cake formation, R_c ; and thickness, δ) of the investigated systems. Experimental conditions were as stated in Figure E.1.

System	α (10^{12} m/g)	d (μm)	ε	R_c (10^{13} m^{-1})	δ (μm)
Alginate	7.86	0.3	0.27	6.28	10.9
Alginate, calcium	2.10	4.7	0.071	4.06	20.8
Alginate, alum	0.89	496	0.004	1.73	19.5
Alginate, calcium, alum	0.67	513	0.005	1.34	20.1

As visually observed, the cake layer formed by alginate solution was not cohesively bounded on the membrane surface (a gentle spray of DI water could remove most of the fouling layer), whereas when calcium and/or alum was present, the cake layer was more cohesively bounded. This implies that the addition of calcium and/or alum enhanced the attachment of alginate on membrane, which is also shown by the cake

layer thickness that increased by almost 2 folds when alum and/or calcium were added.

E.4 Conclusions

Alum and calcium may change the characteristics of alginate fouling layer when introduced into the system. As assessed by the Blocking Filtration Law, the dominant fouling mechanism when alginate and alum are present is cake filtration. The dominant fouling mechanism cannot be clearly distinguished by the Blocking Filtration Law when alum was present since all of the fouling mechanisms co-exist.

The addition of alum and calcium could also change the cake characteristics by decreasing the resistances. While the porosity of the cake decreased, the permeate flux remained higher than when only alginate was present, suggesting that it might not be the porosity that governs the permeability of the cake, but rather the gel network. In addition, the low porosity of cake layer formed by alum-flocculated alginate molecule implies that the cake was compressible. Lastly, the addition of alum and/or calcium resulted in more cohesively bounded alginate on the membrane surface, and as shown by the increased cake thickness.

Appendix F

Coagulation pre-treatment in Nanofiltration: Effects of coagulant concentration, calcium and settling

*Presented at the International Conference on Membranes (ICOM), Hawaii, 2008

F.1 Introduction

Nanofiltration (NF) is now an emerging technology in drinking water treatment and wastewater reuse. The process of employing this membrane is considered very attractive due to its distinctive feature of retaining charged particles down to the size of multivalent ions at a lower pressure compared to that of reverse osmosis (RO). One of the major obstacles in membrane filtration is fouling which may cause decline in both flux quality and quantity, and eventually lead to a shorter membrane life. In addition, divalent cations such as calcium (Ca^{2+}) that are naturally present in raw water may neutralize the negatively-charged organic molecules leading to a dense fouling layer (Tang *et al.* 2007b).

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Natural organic matter (NOM) is considered as a major membrane foulant and is commonly removed in the drinking water treatment train via coagulation/flocculation process with the aid of coagulating agents such as alum; settling then follows this. In this study, we have shown that coagulation as a pre-treatment process of membrane nanofiltration could significantly alleviate flux decline and reduce the specific cake resistance compared to that without pre-treatment, even when calcium ions are present in the system. It is also shown that settling has no significant effects in improving permeate quality and alleviating flux decline. Thus, our findings provide insights to the possibilities of the application of direct coagulation-nanofiltration processes especially in drinking water treatment.

F.2 Materials and Methods

Commercial Pretreated Aldrich Humic Acid (PAHA) is chosen as the organic model foulant for the tests. PAHA concentration is 30 mg/L throughout the experiments. Alum doses are varied from 0-100 mg/L. 1 mM calcium chloride is added when required. Final pH and ionic strength are adjusted to 7 and 10 mM as NaCl respectively. NF-270 membranes (Dow Film Tec) are used in the experiments.

Fouling experiments are conducted in a bench-scale dead-end filtration system as schematically shown in Figure 3.3, which comprises of a reservoir tank (Millipore Corporation, Bedford, MA) with a volume of 800 mL, connected to a stainless steel stirred cell (Millipore Corporation, Bedford, MA) with a volume of 50 mL and houses a 47 mm diameter membrane sample. Pressure is provided by a compressed nitrogen gas tank which is applied to the reservoir tank to give 3.5 Bar of trans-membrane pressure (TMP). Permeate flux is collected and the mass is monitored over time using a weighing scale connected to a data logger. Fouling experiments are conducted for at least 12 hours. Organic concentrations are measured using UV/VIS Spectrophotometer and cation concentrations are measured using Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES). Floc size is measured using Static Light Scattering (SLS). Foulant concentration on the membrane surface is

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determined gravimetrically using base extraction as stated elsewhere (Tang *et al.* 2007b).

F.3 Results and Discussion

F.3.1 Flux trends and resistance analyses

Figure F.1 Flux decline trends of three different systems (only PAHA; PAHA and alum; PAHA, alum, and calcium).

As shown in Figure F.1, the most severe flux decline occurs for feed solution containing only PAHA. When alum coagulant is added, the resulting flux decline is less severe despite more PAHA is accumulated on the membrane surface compared to the system containing only PAHA. Feed solution containing PAHA, alum coagulant, and calcium gives the least flux decline. This is because the resulting flocs are larger when calcium ions are present (Lee *et al.* 2003). According to the Carman-Kozeny Equation, larger particles will result in lower specific cake resistance (Carman 1938).

Total resistance, resistance due to cake formation, and membrane resistance are determined for each system. As shown in Table F.1, system containing only PAHA

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has the largest R_c relative to R_m , followed by PAHA and alum, and PAHA, alum, calcium respectively.

Table F.1 Resistance calculation from the three systems. R_{tot} = total resistance; R_c = resistance due to cake formation; R_m = membrane resistance.

System	$R_{tot} (m^{-1}) \times 10^{13}$	$R_c (m^{-1}) \times 10^{13}$	$R_m (m^{-1}) \times 10^{13}$	$R_c/R_m (-)$
PAHA+Al+Ca	3.99	1.36	2.63	0.52
PAHA+Al	4.48	1.78	2.64	0.67
PAHA	6.14	3.68	2.46	1.49

F.3.2 Effects of alum concentration

When alum concentration is varied from 0 to 100 mg/L in a system containing 30 mg/L PAHA, there exists an optimum coagulant dosage (at 50 mg/L of alum), which gives the least severe flux decline and high PAHA and alum removals (data not shown). In general, as the coagulant concentration increases, flux decline becomes less severe as can be seen in Figure F.2.

Figure F.2 Effects of coagulant concentrations on flux decline.

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One exception is at alum concentration of 100 mg/L where the flux decline is as low as that of 20 mg/L of alum dosage. A possible explanation for this is that although the floc size formed at alum concentration of 100 mg/L is as large as that at 50 mg/L (data not shown), the flocs become denser resulting in higher specific cake resistance (Figure F.3).

Figure F.3 Specific cake resistances obtained for systems with varied coagulant concentrations. Theoretical values are calculated using the Carman-Kozeny Equation.

Addition of alum coagulant with a dosage of more than 10 mg/L in these systems, in general, will decrease the specific cake resistance. At alum concentration of 10 mg/L, the resulting specific cake resistance is higher than that without alum addition despite the lower flux decline. This is due to less PAHA is attached on the membrane surface although R_c is lower, hence, by ratio of R_c to the accumulated mass, the specific cake resistance is higher.

The difference between theoretical and experimental specific cake resistances lies on the assumption made in the Carman-Kozeny Equation. In this equation, it is assumed that all filtered mass will stick on the membrane surface, whereas in these experiments between 1 to 79% of the mass stays on the membrane (data not shown).

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Figure F.4 Effects on settling after coagulation/flocculation on flux decline.

F.3.3 Effects of settling

Two identical feed solutions are used in this experiment. In one set of experiments, a 2-hour settling is conducted after coagulation/flocculation and its supernatant is fed into the membrane filtration system to observe the effects of settling on flux decline. As can be seen in Figure F.4, settling helps to mitigate flux decline by approximately 20%. For both systems, there is no further flux decline after 100 minutes of filtration.

Figure F.5 shows the PAHA and alum removals in both systems. Settling does not significantly improve PAHA removal (from 98.5% to 98.8%), and alum removal remains 100% for both systems. In addition to this, since settling slightly mitigates the flux decline (as seen in Figure F.4), these findings suggest that direct coagulation-nanofiltration may be potential to be applied for NOM removal.

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Figure F.5 Comparison of PAHA and alum removals of NF-270 membranes when settling was conducted after coagulation/flocculation.

F.4 Conclusions

- Addition of alum coagulant for PAHA removal in nanofiltration alleviates the flux decline and improves the permeate quality.
- Settling after coagulation/flocculation does not significantly improve the permeate quality and quantity.
- Direct-coagulation nanofiltration for removal of NOM is potential to be applied in drinking water treatment.

List of Publications

Journal Publications:

1. Listiarini, K., Sun, D.D., Leckie, J.O., 2009. Organic fouling of nanofiltration membranes: Evaluating the effects of humic acid, calcium, alum coagulant and their combinations on the specific cake resistance. *Journal of Membrane Science*. 332, 56-62.
2. Listiarini, K., Chun, W., Sun, D.D., Leckie, J.O., 2009. Fouling mechanism and resistance analyses of systems containing sodium alginate, calcium, alum and their combinations in dead-end fouling of nanofiltration membranes. *Journal of Membrane Science*. 344, 244-251.
3. Listiarini, K., Tor, J.T., Sun, D.D., Leckie, J.O., 2010. Removal of bromide and bromate in waters containing humic acid by Hybrid Coagulation-Nanofiltration Technique. *Journal of Membrane Science*, 365, 154-159.
4. Listiarini, K., Tan, L.H., Sun, D.D., Leckie, J.O., 2011. Cross-flow nanofiltration of sodium alginate, calcium, alum and their combination: calcium-alginate interaction. *Journal of Membrane Science* (in press).

Conference Publications:

1. Listiarini, K. Sun, D.D., and Leckie, J.O., 2008. Coagulation pre-treatment in nanofiltration: Effects of coagulation concentration, calcium and settling. *International Conference on Membrane (ICOM) 2008*, Honolulu, USA, 12-18 Jul. 2008.
2. Listiarini, K., Sadreddini, S., Sun, D.D., and Leckie, J.O., 2008. Organic fouling of nanofiltration membranes: Force measurements of organic foulants in systems

containing coagulant and divalent cations. IWA World Water Congress and Exhibition 2008, Vienna, Austria, 7-12 Sep. 2008

3. Listiarini, K., Wei, C., Sun, D.D., and Leckie, J.O., 2009. Fouling mechanisms of nanofiltration of sodium alginate, calcium, alum and their combinations: Blocking Filtration Laws and Membrane Fouling Index, IWA Leading Edge Technology Conference 2009 at the Singapore International Water Week (SIWW), Suntec City, Singapore, 22-26 Jun. 2009.

4. Listiarini, K., Sun, D.D., Leckie, J.O., 2009. Cake characterization of sodium alginate fouling of nanofiltration membranes in the presence of calcium and alum. IWA International Chemical Specialists Conference, Water and Industry 2009, Palmerston North, New Zealand, 30 Nov. - 2 Dec. 2009.